

Selection and Use of
Polymers in Contact Filtration

Missouri Water Resources Research Center
Columbia

Prepared for

Office of Water Research and Technology
Washington, DC

Feb 80



U.S. Department of Commerce
National Technical Information Service

NTIS

SELECTION AND USE OF POLYMERS IN CONTACT FILTRATION

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University of Missouri

PROJECT NUMBER: A-107-MO
Agreement Number: USDI-OWRT-14-34-0001-8027 and 9027

Dates: March, 1978 - September, 1979

COMPLETION REPORT
February 1980

The work upon which this publication is based was supported in part by funds provided by the Office of Water Research and Technology (A-107-MO), U.S. Department of the Interior, Washington, D.C., as authorized by the Water Research and Development Act of 1978.

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A-107-MO (1)

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BIBLIOGRAPHIC INFORMATION

PB80-160351

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Feb 80

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PERFORMER: Missouri Water Resources Research Center,
Columbia.
Contracts DI-14-34-0001-8027,
DI-14-34-0001-9027

SPONSOR: Office of Water Research and Technology,
Washington, DC.
W8004018 OWRTA-107-MO(1)
Completion rept. Mar 78-Sep 79

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KEYWORDS: *Water treatment, *Polymers, *Filtration.

Available from the National Technical Information Service,
Springfield, Va. 22161

PRICE CODE: PC A07/MF A01

Selected Water Resources Abstracts Input Transaction Form		3. Accession No. W 80-04018	
4. Title Selection and Use of Polymers in Contact Filtration, <i>all caps</i>		5. Report Date 6. Performing Organization Report No.	
7. Author(s) Ghosh, Mriganka M. and Yeh, H-H.		10. Project No. OWRT A-107-MO (1)	
9. Organization Dept. of Civil Engineering University of Missouri-Columbia Columbia, Missouri		11. Contract/Grant No. 14-34-0001-8027 and 9027	
15. Supplementary Notes Completion Report , Missouri Water Resources Research Center, University of Missouri, February 1980, 134 p, 53 fig, 11 tab, 41 ref			
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17a. Descriptors *Water treatment; <i>direct</i> *filtration; *polymer; <i>selection</i> ; dosage selection; <i>Cation exchange</i> ; <i>density</i> ; velocity gradient; head loss; floc breakup; high shear; <i>Turbidity removal</i> ; <i>Polyelectrolytes</i> .			
17c. COWRR Field & Group VP OSF			
18. Availability the National Technical Information Service as PB PB 80 16039		20. Security Class. (if any) 21. No. of Pages 22. Price Send to: Water Resources Scientific Information Center OFFICE OF WATER RESEARCH AND TECHNOLOGY U.S. DEPARTMENT OF THE INTERIOR Washington, D.C. 20240	
Abstractor Mriganka M. Ghosh		Institution University of Missouri-Columbia	

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Chapter 1

INTRODUCTION

New drinking water standards, new particulates found to exist in some waters and expanded sludge disposal problems created by new water pollution control requirements, have caused engineers to look into innovative treatment methods involving the use of synthetic polyelectrolytes in water treatment. The conventional method to remove colloidal and other solids from water consists of flocculation, sedimentation, and rapid filtration of floc through granular media. Most natural waters can be regarded as dilute suspensions which, from a kinetic standpoint, respond poorly to conventional flocculation using hydrolyzed metals. A promising alternative to the conventional method of turbidity removal is the direct or contact filtration using synthetic polyelectrolytes as coagulants in dual or multi-media filters.

In the direct filtration process, the water is treated with an organic polyelectrolyte by rapid mixing and then directly applied to the filter. The absence of flocculation and sedimentation tanks represents a significant saving in terms of plant size and capital investment. Further, the use of polyelectrolytes in place of metal coagulants may reduce substantially the amount of sludge to be handled. Essentially, the only sludge that results from such an operation is that obtained from the treatment of backwash water. The process is particularly attractive when polymeric coagulants are used because the floc deposited in the filter bed is significantly less in both mass and volume than when hydrolyzing metals are used. The sludge is composed almost entirely of particulate matter removed from the water. This not only represents a considerable savings in energy but also a reduction in operational problems.

The current interest in the use of polymeric coagulants for water treatment processes generally stems from: (1) the new drinking water turbidity level being set at 1 turbidity unit instead of 5 with the possibility of its being lowered again to meet the goal of 0.1 turbidity unit proposed by the American Water Works Association, (2) presence of new particulates in large concentrations in surface waters causing treatment problems, e.g., in waters contaminated with asbestos fibers, both negatively charged amphibole and positively charged chrysotile may occur simultaneously; same chemical treatment and same filtration system may fail to provide removal of these two types of particles with equal effectiveness, and (3) problems encountered in disposal of sludges of hydrated metal oxides resulting from conventional treatment. Polymers are used as primary coagulants in flocculation, with or without hydrolyzing metals, in direct or contact filtration, both in pre-conditioning of water-and coating of filter media, and for conditioning of sludges.

Very little attention has been paid to date to developing a rational procedure for the selection of the "right" polymer for a specific job in water and wastewater purification. Most often the selection of polymer is made on a "hit or miss" basis. There is no rational method for selecting a polymer for a given job from more than two thousand polymers that are commercially available. The selection of polymer is a critical step in contact filtration simply because the clarity of the treated water will depend in large measure on the successful polymer-preconditioning of the water. Of equal importance in polymer performance is the role of the mixing step.

Polymers, pH and ionic strength are the three important variables that can be used in various ways to improve the efficiency of direct filtration by modifying the surface characteristics of either the suspension, filter or both and making use of the bridging mechanism. These are: (1) increasing the rate of deposition, (2) extending the depth of penetration for better utilization of the entire bed depth, (3) increasing the removal capacity of the bed, and (4) minimizing headloss and preventing premature clogging. The selection of a suitable polymer depends on the weight given to each of these aspects and also the type of chemical bonding between it and the surface which is enhanced by the operating pH and ionic strength.

The present rate of progress with synthetic polymers would be improved significantly by a more enlightened attitude on the part of some manufacturers. The minimum information that should be supplied by the manufacturers should include (1) type of polymer or copolymer, (2) concentration of active ingredient, (3) concentration of free monomer, (4) proportion of ionizable groups, and (5) molecular weight or intrinsic viscosity under specified conditions. With this information on hand, success and failures in the laboratory and in the field would be meaningful and contribute to the technology of water clarification.

Research Objectives

The objectives of this investigation are as follows:

1. To develop a simple, economical, and reliable method for the selection of polymers for use in direct filtration of natural suspensions.
2. To obtain sufficiently broad-based data on direct filtration of selected dilute suspensions, representing most natural waters, using polymers ideally suited to direct filtration.

Scope

The methods investigated for selecting polymers for filtration were all primarily based on polymer-particle interaction. Several polymers of varying molecular weights and charge characteristics and two natural suspensions, namely bentonite clay and mixed metal hydroxide suspensions, were used throughout the study. The techniques tested for measuring polymer-particle interactions were change in viscosity, conductivity, electrokinetic potential (zeta potential), and charge density, as measured by colloid titration. The reduction in titrable colloidal surface concentration was measured both by measuring turbidity and particle size distributions using a HIAC particle counter.

Additionally, refiltration technique was used to determine the extent of surface coverage of bentonite clay at various dosages of polymers of different molecular weights and charge characteristics. The extent of coverage, in turn, were correlated with the resultant quality of filtered water. An important aspect of polymer use in water clarification is the role of mixing. This was thoroughly investigated in order to determine the minimum shear (velocity gradient, G) and time of mixing required in obtaining the optimum filter run, measured by acceptable filtrate quality and head loss. On the other hand, it was also important to obtain a quantitative estimate of floc strength since, in many filter runs, after a certain extent of clogging causing high shear within pore spaces, floc break-up might occur. This results in poor filtrate quality. Floc size distribution were measured following various mixing times and intensities.

Chapter 2

RELATED RESEARCH AND CURRENT KNOWLEDGE

Use of Polymers in Water Treatment

Experience has shown that the use of polyelectrolytes is perhaps the key to solving many of the problems facing the water industry. Polyelectrolytes may be used as primary coagulant in flocculation or in contact filtration, as flocculation or filter aids, for precoating filter media and as sludge conditioners. Focussing on filtration, Hunter and Alexander (1) showed that by reversing the surface charge on silica sand from negative to positive by adsorption of hexadecyltrimethylammonium ions it was possible to increase significantly the ability of the sand column to remove negatively charged kaolinite particles from suspension. Conley and Pitman (2) observed that the application of polyacrylamide, a nonionic polymer, improved the filterability of alum floc by sand columns and postulated that the polymer helped in binding the floc particles to each other and the filter medium. Different mechanisms may bring about particle aggregation and attachment using polymers. One of the main advantages of polymers in comparison with hydrolyzing metals, such as alum, is their capacity for adsorption and interparticle bridging. Adin and Rehman (3) have shown that better performance in contact filtration of low-turbidity waters stems from the sorptive and bridging properties of polymers. Despite the widespread use of polymers no information exists in the literature on the method of selecting polymers for use in water works.

Polymer Adsorption and Destabilization

The extended-segment model of polymer adsorption on solid surfaces was first proposed by Jenckel and Rumbach (4) and later a sound theoretical framework was developed by Simha, Frisch and Eirich (5). In this model the polymer molecule is attached to the adsorbent surface by a fraction of the total number of segments

comprising the polymer chain. This model reduces to Langmuir's adsorption isotherm when the number of adsorbed segments reduces to one. The mechanisms of destabilization of colloidal dispersions can be divided into two categories: (1) processes which effect a net reduction of potential energy of interaction between two similar double layers, and (2) processes which enmesh colloidal particles in a three-dimensional floc mesh formed by chemical bridging. La Mer (6) designated the first group as coagulation and the second as flocculation. With low to medium weight (molecular weight = 10,000 to 200,000) polymers the aggregation of silica dispersions, such as bentonite clay, may be accomplished by either or both coagulation and flocculation as designated by La Mer, depending on the concentrations of clay and polymer, and the pH. Since in the clay-polymer system a sharp distinction cannot always be made, the term coagulation may be used to define all cases exhibiting particle aggregation. However, the transition between the physical double-layer model and polymer bridging theories is bridged by the "adsorption coagulation theory" since both electrostatic interaction and chemical adsorption participate in the destabilization process. Stoichiometry between coagulant dosage and colloid surface is possible, but may not always occur. Also, the aggregates can exhibit widely varying shear strength, density, and filterability.

In the bridging mechanism, anionic and nonionic polymers attach to negative surfaces via H-bonding, anion interchange with adsorbed anions, or interaction with cations in the diffuse double layer.

Polymer Adsorption Model

A predictive theoretical model for the adsorption of a flexible random coil polymer was first proposed by Simha, Frisch, and Eirich (SFE)(5). The model, although, has undergone various modifications, basically describes the equilibrium between the sorbate polymer concentration and the sorbent colloid

surface as shown below:

$$\frac{C_a}{S} = \Gamma = \frac{\Gamma_m K C_e}{1 + K C_e} \quad (1)$$

where

C_a = conc. of polymer adsorbed, mole/l

C_e = conc. of residual polymer in solution, mole/l

S = conc. of colloid surface, m^2/l

K = equilibrium constant for the adsorption-desorption reaction

Γ_m = ultimate adsorption capacity of colloidal surface, mole/ m^2

If the total concentration of polymer required to produce a certain fractional coverage θ of the colloid surface is expressed by $C_{t\theta}$ then, it can be shown from Eq. 1 that

$$C_{t\theta} = \frac{\theta}{K(1-\theta)} [1 + K S \Gamma_m (1-\theta)] \quad (2)$$

given that

$$C_{t\theta} = C_e + C_a$$

and

$$\frac{C_a}{S} = \theta \Gamma$$

When $C_a > C_e$ and $C_{t\theta} \approx C_a$, Eq. 2 reduces to

$$C_{t\theta} = \Gamma_m S \theta \quad (3)$$

So, when most of the added polymer is adsorbed dosage is linearly related to surface concentration. On the other hand, if most of the polymer added remains in solution (adsorption is minimum)

$$C_a < C_e$$

$$\text{and } C_{t\theta} = \frac{\theta}{K(1-\theta)} \quad (4)$$

and the dosage is independent of surface concentration. Actually, C_{t0} varies with S^n where $0 \leq n \leq 1$, where Γ_m and K are characteristics of the dispersed colloidal phase (sorbent), the dispersion medium (water), and the sorbate (polymer).

Optimum Polymer Dose

The most common way of determining polymer dosage for particle separation processes, such as flocculation or direct filtration is by use of the jar test procedure. The dosage is conceivably a function of colloid concentration, the characteristics of the dispersion medium such as pH and ionic strength, the characteristics of the polymer, such as its molecular weight, ionizable groups, charge density distribution at various pH's, and the polymer mixing intensity, measured by mean velocity gradient G and time of mixing, t . The effect of mixing time is not very significant for times larger than 2 to 3 minutes, as shown by Camp (7). However, the effect of G on polymer dosage has been documented well by Morrow and Rausch (8), Letterman et al (9) and Camp (7).

Several other techniques, namely (1) prediction of dosage from the charge neutralization standpoint, (2) measurement of variation in electrokinetic potential (zeta potential), and (3) refiltration method. The first two methods depend on the premise of double layer modification through charge neutralization. In method 1 above, colloid titration of polymer as well as the sorbent dispersion play a key role in determining dosage as shown by Toei and his coworkers (10)(11) and Kawamura and Hannah (12).

Various predictive models have been proposed to describe the relationship between zeta potential of the dispersed colloidal phase and the concentration of destabilant polymer. Recently, Wnek and Davies (13) showed that zeta potential versus concentration curve can be predicted mathematically by using

a multicomponent adsorption isotherm in conjunction with a relationship between zeta potential and surface charge. As expected, ionic strength exhibited a strong influence on surface charge distribution as a function of pH.

Role of Molecular Weight and Charge Density of Polymer

Lindquist and Stratton (14) reported on the role of molecular weight (MW) and charge density on the adsorption and flocculation of colloidal silica with the cationic polymer polyethylenimine (PEI). Up to the concentration of PEI required to initiate coagulation (critical coagulant concentration, ccc) virtually complete adsorption of polymer occurred regardless of molecular weight, pH, and ionic strength. That is, Eq. (3) was applicable at ccc dosage. However, if $C_{t\theta} > ccc$, Γ_m increased with MW of PEI, pH or ionic strength. The flocculation results indicated that at pH 9 or greater, polymer bridging is the dominant mechanism of destabilization since PEI charge density is quite low at these pH's. At pH less than 9, charge interaction between negatively charged colloidal silica and cationic PEI (MW = 1760 to 18,400) was definitely the dominant mechanism. Also, regardless of MW, logarithm of molar ccc exhibited an inverse linear relationship with the charge density of PEI. Needless to add that such a relationship is also pH independent. In general, ionic strength has a small effect on surface charge density of silica or PEI, although the intrinsic viscosity of the polymer is lowered considerably by the addition of a salt. The relationship between ccc in mole/l and cationic charge/molecule of PEI is given by

$$(ccc)_{\text{molar}} = h/z^a \quad (5)$$

where z = number of cationic charges per molecule of PEI

h = ordinate intercept of the log-log plot

a = slope of log-log plot

The value of a was 0.94 in the absence of NaCl and 0.71 in the presence of 0.1N NaCl. It clearly indicated that the flocculating ability of PEI molecules of differing weight-averaged molecular weights, $\langle M \rangle_w$ or under differing pH conditions are not due to size or chain length, but rather to charge density, z .

The adsorption of PEI on silica can be described by "monolayer" of polymer yielding a Langmuir type isotherm as shown by a modified form of Eq. 1.

$$S \cdot \frac{C_e}{C_a} = \frac{1}{\Gamma_m K} + \frac{C_e}{\Gamma_m} \quad (6)$$

In all cases, Γ_m decreased with pH and ionic strength. Further, Γ_m increases somewhat with $\langle M \rangle_w$ at constant pH (15).

$$\Gamma_m = K' \langle M \rangle_w^p \quad (7)$$

where p lies between 0 and 1 if Γ_m is expressed in weight of polymer per unit area of colloidal surface.

Optimum Polymer Dose from Refiltration Theory

Smellie and La Mer (16) observed that the flow rate Q during refiltration of flocculated suspension was universally proportional to the square of the surface area of particles in a unit volume of filter cake, S_0

$$Q = K_f S_0^2 \quad (8)$$

Also, the dosage of coagulant needed at maximum refiltration rate was directly related to S_0^2 . It was proposed that rate of floc formation was proportional to the product of primary nuclei covered with polymer, $N_0\theta$, and nuclei with open surface, $N_0(1-\theta)$, in accordance with a bimolecular process

$$\frac{dn_0}{dt} = k_1 n_0^2 \theta (1-\theta) \quad (9)$$

and rate of floc disintegration

$$\frac{dn_o}{dt} = k_2 R^3 / \{ R^{2\theta} (1-\theta) \} \quad (10)$$

where R = radius of floc. At equilibrium,

$$R = k_1 n_o^2 \theta^2 (1-\theta)^2 / k_2 \quad (11)$$

Assuming r = radius of primary particle, Q_o = filtration rate of untreated suspension when $\theta = 0$. Then from Eqs. 8 and 11,

$$Q - Q_o = Q_o k_1^2 w^4 \theta^4 (1-\theta)^4 / r^2 k_2^2 \quad (12)$$

where w = solid content of suspension.

Equation 12 states that for $\theta = 0.5$, i.e., $\theta^4(1-\theta)^4 = \frac{1}{256}$ leads to a maximum in $Q - Q_o$. When no polymer is adsorbed ($\theta=0$) or colloid surface is fully covered ($\theta=1$) and no bridging can occur, dn_o/dt in Eq. 10 approaches infinity. Therefore, conceptually, $\theta=0.5$ gives the optimal coverage and maximizes the refiltration rate Q . It can also be seen from Eqs. 8 and 11

$$C_o^{1/2} / (Q - Q_o)^{1/8} = a + p C_o \quad (13)$$

where C_o = polymer dosage. A plot of Eq. 13 yields a straight line with a slope and intercept of p and a , respectively, and the optimum polymer dosage is given by

$$C_{opt} = \frac{a}{p} \quad (14)$$

Floc Strength Under Hydrodynamic Forces

The term "flocculation" in this section will imply the use of water-soluble polymers which are adsorbed on the particles and provide material bridges. The essential function of polymeric flocculants is to produce large aggregates ("flocs") which will settle rapidly and/or will be strong enough to withstand subsequent passage through deep filters. Suspensions "coagulated" with simple

electrolytes are generally slow-settling and difficult to filter. When the polymeric flocculant is used, aggregation proceeds at a rate controlled by inter-particle collisions until a quasi-steady state is reached at which the rate of growth equals the rate of breakdown, at least for short periods. The strength of the flocs is therefore reflected by the average size which persists in an agitated suspension. The mean velocity gradient, G , is taken as a measure of the shearing stress as shown below

$$T = \mu G \quad (15)$$

where T is in dynes/sq cm and μ is in poise (dyne-sec/sq cm). The shearing stress corresponding to a G of $10,000 \text{ sec}^{-1}$ in water at 25°C (viscosity 0.896×10^{-2} poise) is 90 dynes/sq cm. This indicates that the shear stress to which flocs are subjected in an average flocculation basin ($G = 10$ to 70 sec^{-1}) is extremely small. This stress at $G = 10,000 \text{ sec}^{-1}$ is equivalent to an energy of 90 dyne-cm/cc, or 2.15×10^{-9} kcal per cc of water, or 4.8×10^{-8} kcal/mole of water. As the bond energy associated with weak van der Waals forces or hydrogen bonds (about 5 kcal/mole) is 10^8 times this magnitude, it is reasonable to assume that shear is not the mechanism of floc breakup. The forces holding the floc particles together is probably interfacial tension. The surface tension of water in contact with air is about 72 dynes/cm at 25°C . The surface tension of a floc particle must be higher than 72 dynes/cm, so that the interfacial tension (or difference) is adequate to withstand the shear forces accompanying G (7).

Tomi and Bagster (17) developed a relationship between maximum stable size of floc and G as shown below

$$d_{\max} \propto G^{-.5} \quad (16)$$

The order of dependence of $d_{\max}$ reported by Smith and Kitchner (18) for flocculation carried out in a couette type device was -0.2. Letterman et al (19) attempted to develop a method for predicting an optimum combination of G and t for rapid mixing for a predefined minimum residual turbidity. The existence of an optimum t for all values of G tested, as measured by residual turbidity, suggested that the early conditions of floc formation are important and the function of rapid mix operation is more than simply to disperse the flocculant. The relationship between G, t, and dosage C of alum for a constant residual turbidity was expressed as

$$\log(Gt) = k - m \log C \quad (17)$$

where K and m are constants.

The Direct Filtration Process

Deep bed filtration is a subject which has, in recent years, developed a rich and varied literature. Despite the dramatic progress in our understanding which this has produced, a comprehensive method capable of predicting the dynamic behavior of filter over its entire operational span has remained out of reach. No doubt the uncertainties surrounding some aspects of the deposition process pose the greatest hindrance towards a general predictive model.

Deep bed filters are being used for the tertiary treatment of wastewaters in addition to being used in various modified forms for the purpose of water filtration. The problem of providing more water of higher quality has provided the impetus for the development of new technology in water filtration. Direct high rate filtration of low turbidity waters is an attempt to that end. Usually coarser grain diameter to reduce headloss and the injection of a polymeric flocculant just before water enters the filter, to promote particle attachment

to filter grains, are prerequisites to direct filtration. Since flocculation in such a case occurs during contact with the filter medium, the process may be called "contact flocculation-filtration" (20). Cationic polyelectrolytes of low to medium molecular weight seem to be most effective in the direct filtration process, especially in dual or multimedia filters treating natural suspensions (20)(21). Interparticle bridging between filter grain and filtered particle is the dominant mechanism by which a polyelectrolyte functions in direct filtration, according to Habibian and O'Melia (22). Cationic polymers may be used as the sole flocculant permitting larger rates of filtration in coarse-grain beds with detriment to filtrate quality or a reduction in the volume filtered per cycle. Further, with polymers the volume of backwash sludge is much less compared to hydrolyzing metal coagulants.

Tate (23) et al. used pilot plant tests to study the possibility of using direct filtration to treat the water from Deers Creek Reservoir, Utah. Both alum and cationic polyelectrolyte were used as coagulant, the premixing intensity G was 100 sec^{-1} and the results indicated equivalent turbidity value and particle removals for direct filtration and conventional treatment process. They also showed no difference on water quality parameters between 13 and 26 min. flocculation time.

Hutchison (24) et al. showed that for a constant filtration rate, alum dosage, and velocity gradient, G , an increase in flocculation time resulted in a decrease in the length of filter runs. This suggested that flocculation time requirements were perhaps less than 10 min. Hutchison (25) also showed that with higher values of G , there was an increased likelihood of filter breakthrough. However, there was some evidence of a smaller floc volume. This was indicated by the longer time it took the filter to reach a certain level of headloss at the

higher flocculation mixing intensity. For the three different filter coal sizes studied, the findings reveal that the longer the flocculation period beyond 4.5 min., the greater the likelihood of turbidity breakthrough.

Glaser (26) et al. studied the coagulation and direct filtration of humic substances with polyethylenimine (PEI). They found that the removal efficiency of the filters operated at the optimum dosage increased with increasing molecular weight of the polymer when a reasonable flocculation period was provided. Without flocculation, no effect of the molecular weight of polymers on filter efficiency was apparent. The data also showed high headloss for smaller humic acid flocs which could be reduced by providing some flocculation. Stump (27) showed that flocculation period made a significant difference in the performance of a polymer. A flocculation period of twenty minutes or longer was found to be effective. Treweek (28) showed that for a Gt values equal to or greater than 42,000, direct filtration was effective in removing all aggregates larger than $7.5 \mu\text{m}$ in size. The experiments also indicated that a flocculation time shorter than 7 min. was not sufficient to produce the aggregate of the singlets required for their removal within the filter media.

Mechanistic Models for Contact Filtration

The flow of suspensions through porous media is a complex phenomenon due to the diversity of mechanisms involved. The prerequisite to the optimization of deep, granular filter design is a reliable mathematical description of the capture of suspended particles by packed collector grains within a flow. In the last decade major effort in filtration research has been directed toward developing a comprehensive theory correlating all variables affecting the process. The capture of particles from low velocity flows in porous beds is believed to involve two distinct steps, namely, particle transport and attachment (29). Particle transport is obtained by physical forces, such as gravity with interception as the boundary

condition, hydrodynamic perturbations near the collector media grains, and inertia, among others. Attachment of particles is influenced by surface forces, such as coulombic forces of electric double layers at the solid-liquid interface and London-van der Waals forces (30). An excellent review of the various physical and chemical mechanisms that may perhaps be operative in granular filters was given by Herzig et al. (31).

Spielman and Fitzpatrick (32) developed a theory of filtration of non-diffusing particles based on solution of trajectory equations for motion of a small particle near a much larger collector considering gravity, hydrodynamic, attractive and repulsive forces simultaneously. Ghosh et al. (27) extended this model to include the filtration of diffusive particles. This model is particularly suited to contact filtration systems where the suspension and the filter medium are pretreated with polyelectrolytes to reduce the double layer forces to negligible levels.

The basic model is shown below

$$\eta/\eta_i = \frac{16}{3\pi} \left(\frac{3}{2} \frac{kT}{Q} \right)^{2/3} \left(N_{AD} \right)^{2/3} + f_i(N_{AD}, N_{Gr}) = \frac{\lambda}{\lambda_i} \quad (18)$$

in which

$f_i(N_{AD}, N_{Gr})$ is given by Spielman and Fitzpatrick (32) and it represents the effect of gravity and adhesive forces symbolized by the dimensionless numbers N_{Gr} and N_{Ad} , λ/λ_i represents dimensionless filter coefficient, η/η_i represents dimensionless single collector efficiency, k is Boltzmann's constant, T is absolute temperature ($^{\circ}K$), and Q is Hamaker constant. The subscript i refers to either filter coefficient or single collector efficiency (see Eqs. 2 and 3 below) considering interception as the sole filtration mechanism. The filter coefficient λ is the proportionality constant in the first order removal of particulates along depth in a granular bed as shown in Eq. 19

$$-\frac{dn}{dz} = \lambda n \quad (19)$$

in which n is the numerical concentration of particles and z is the depth of bed. The relationship between filter coefficient λ and the single collector efficiency η is given by

$$\lambda = 1.5 \left(\frac{1-f}{d_s} \right) \eta \quad (20)$$

in which f is the fraction of voids in the granular bed consisting of grains of geometric mean size, d_s . The dimensionless single collector efficiency, η , is defined as the ratio of particles striking the collector to the total particle flux to the collector. This model, along with many other similar ones, is appropriate for the prediction of efficiencies only during early periods of filtration. The adequacy of the model in predicting the removal of particulate matter from dilute suspensions has been demonstrated by Ghosh and his co-workers (33)(34).

Various empirical or semiempirical predictive models are available in the literature to describe kinetics of removal in "clogging" filters. However, because of the complicated and somewhat conservative approach of these models, they have failed to provide the simple mathematical tools required for the analysis, comparison, and design of direct filtration processes. Among these studies on modeling, the study of Herzig et al. (25) is particularly noteworthy in that it includes a method to reduce the pertinent equations, macroscopic material balance and rate equations, to a set of two ordinary differential equations whose solution can be carried out without complicated algorithms. All dynamic models for clogging filters contain adjustable parameters that must be determined experimentally. Notably different from these semiempirical models are the two recent studies the first of which was reported by Wnek et al. (35) that attempts to simulate filter performance on a truly predictive basis. As part of the phenomenological description, a charge balance was made in order to account for the altered surface interaction resulting from the deposition of colloidal matter. However, the assumption that particle

deposits form a relatively smooth coating around filter grains is a debatable deposit morphology for noncolloidal suspensions. The second study has been reported by Tien et al. (36). The dynamic behavior of a filter during the entire filtration cycle was modelled using a two stage deposit morphology: a first stage dominated by deposition according to smooth coating around collector grains which continues until the specific deposit attains a transition value, followed by a second stage corresponding to transition to deposition by the constriction clogging mode. The first mode of deposition results in increase in grain diameter, decrease in porosity, and an increase in pore velocity. The second mode of deposition results in an decrease in the number of unit constriction cells available for flow and this continues until specific deposit reaches an ultimate value corresponding to the onset of nonretentivity or reentrainment of deposited matter.

Chapter 3

EXPERIMENTAL METHODS AND MATERIALS

1. Polymers

The polymers which were evaluated at different phases of this study are listed in Table 1. The functional groups and molecular weights are listed for the polymers for which information was available.

Several measurements were made to determine the extent of polymer-particle interactions. These included measurements of viscosity, conductivity, colorimetry, charge density by colloid titration, electrophoretic mobility (zeta potential), and jar tests.

2. Viscosity

Polymer solutions are pseudoplastic (apparent viscosity decreases with shear rate) while solid suspensions are dilatant (viscosity increases with shear rate). Although these findings are based on high solids and polymer concentrations, a change in viscosity may be detectable even at small concentrations if measurements are made carefully. Change in viscosity may be correlated with amount of polymer adsorbed. A Fischer-MacMichael viscosimeter of the rotating spindle type was used to measure viscosity of 0.2% solutions of different polymers at 25°C and was compared with turbidity removal from a given suspension using these polymer solutions.

3. Conductivity

Electric conductivity of a colloidal suspension is inversely proportional to the colloidal electric potential. Therefore, conductivity of water may change by the addition of a polymer as a function of the colloidal potential of the suspension, besides the usual change expected by the addition of an electrolyte.

Table 1
Characteristics of Polymers

Polymer Name	Type	Molecular Weight	Structure
Corcat P-12	Cationic	1,200	Polyethylenimine
Corcat P-200	Cationic	2×10^4	Polyethylenimine
Corcat P-145	Cationic	4×10^4	Polyethylenimine
Betz 1190	Cationic	5×10^4	Polyamide
Cat-Floc	Cationic	1×10^5	Polydiallyldimethylammonium (PDA DMA)
Betz 1160	Cationic	3×10^6	Organic copolymer of acrylamide
Percol 751	Cationic	5×10^6	Acrylamide based polymers
Percol 757	Cationic	High	Acrylamide based polymers
Betz 1180	Cationic	$\sim 2 \times 10^4$	Polyamide
Betz 1100	Anionic	5×10^6	Copolymer of acrylic acid and sodium acrylate

The conductivity measurement has found some limited application in the control of coagulant dosage and has been suggested as a method of control of algae, hardness and phosphate flocculation (37).

4. Colorimetry

A specific organic dye, such as methylene blue, may be used to determine the extent of polymer adsorption by taking the ratio of its removal from solution by particles with or without polymer coating. A good surfactant should adhere to a particle surface thus resisting other substances from also adhering to it. The magnitude of this resistance, measured by the disappearance of color, will depend on the ratio of concentration of the polyelectrolyte to the surface area of particles. Such an interaction can be detected by a colorimeter or a spectrophotometer.

The first step of the test was to make up a standard calibration curve of a methylene blue solution using a spectrophotometer. Then a known clay solution was mixed with a known methylene blue solution and filtered through a Millipore filter. A correction was made for the amount of methylene blue adsorbed on the filter paper. The amount of methylene blue adsorbed on a known amount of clay could then be determined. Next, a polymer was added to the clay solution and the same procedure repeated. From the difference in the two steps, the amount of polymer adsorbed by the clay was determined.

Various problems were encountered in this method leading to large experimental errors. First of all, the Millipore filter paper and the glass filter adsorbed a large amount of methylene blue. Because the amount of methylene blue adsorbed on the clay particles was very small, experimental errors were large. Another complication in this test was the clogging of the filters. By running a sample of clay solution through 0.3 micron filter paper, 90% of the

clay was retained without much problem with clogging. Upon addition of even a small concentration of polymer (1 mg/l) the filter paper clogged. Various techniques were tried to prevent clogging but not with much success. Because of these problems this technique was abandoned.

5. Electrophoretic Mobility and Zeta Potential

In order to measure the electrophoretic mobility of a colloid particle, a commercial instrument (Zeta meter by Zeta-Meter, Inc., New York) was used. In the usual procedure, a sample of the suspension was placed in a cell under a microscope. Under the influence of a voltage applied to electrodes at each end of the cell, the charge particles will move to the electrode having opposite polarity. The particle velocity can be measured by noting the time it takes particles to traverse a known distance. Then the electrophoretic mobility can be calculated from particle velocity, cell length, applied voltage, and dielectric of the medium.

In order to test how various polymer dosages affect the electrophoretic mobility of bentonite suspension, various amounts of polymer were added into a definite volume of bentonite suspension separately. After 2 min. rapid mixing with a magnetic stirrer, a sample was withdrawn and the electrophoretic mobility measurement procedures specified above were followed.

6. Coagulation Studies

Six-place laboratory stirrer (Phipps & Bird, Inc., Richmond, Va.,) was used for this study. After adding the different amount of polymer solution into each beaker which contained the colloid suspension, the current was turned on and the speed of the paddle set to about 85 rpm for one min. of rapid mixing, then the speed was reduced to about 25 rpm for 20 min. of slow mixing. After

that the stirring was stopped. A further 30 min. of quiescent settling was permitted, then a sample of the supernatant of each beaker was withdrawn for turbidity measurement by HACH Turbidimeter, Model 2100A.

A separate single 3.7-l volume coagulation chamber equipped with variable speed impeller was used for studies to measure the influence of velocity gradient, $G(\text{sec}^{-1})$, determined from impeller speed N , and net torque T_q as shown in Eq. 21

$$G = \sqrt{\frac{2T\pi NT}{60V\mu}} \quad (21)$$

where N = Impeller rotational speed (rpm)

T = Net torque (ft-lbf)

V = Volume of fluid (ft^3)

μ = Dynamic viscosity of fluid (lbf-sec/ft^2)

For a given system, G is proportional to $N^{3/2}$ in accord with Eq. 21.

Torque measurements were made by mounting a torquemeter (Model 783-C-10, Power Instruments, Skokie, IN.) between the motor and mixing paddle. The torque and the rotational speed of the paddle were read with the help of a stroboscope. The speed of the gear end of the motor drive (Model 4555-20, Cole-Parmer Instrument Co., Chicago, Ill.) could vary from 0-150 rpm, and 0-3000 rpm for the direct end. The shaft mounted torquemeter operated between one and ten oz-inches. The calibration curve for G (sec^{-1}) versus N (rpm) is shown in Figure 1. After mixing the polymers with bentonite suspensions at a specific G value for a definite period, the floc size distributions were measured by an automatic particle size analyzer (Model PC-320, HIAC Instruments Division, Pacific Scientific Company, Montclair, CA.).

The HIAC particle counter measures the size of particles in fluid suspensions by using the principle of light blocking. Particles in fluid suspension flow through a channel past a window whose area is known accurately. A collimated light

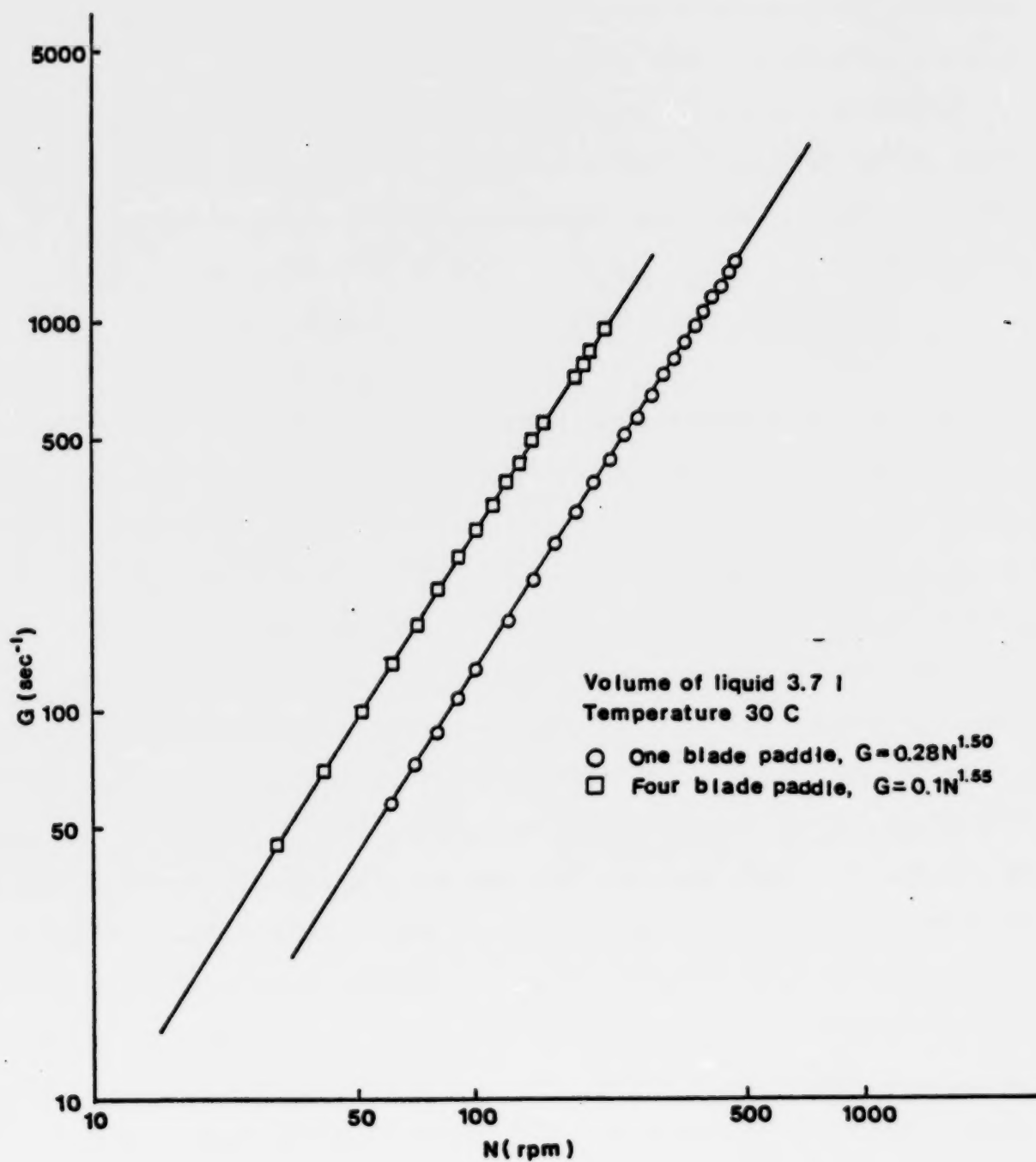


Fig. 1. Relationship Between Velocity Gradient (G) and Impeller Speed (N)

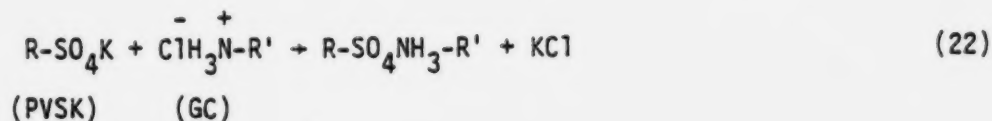
beam shines through the fluid at right angles to the direction of flow, and passes through the window to fall on a photodiode. The output of the photodiode goes to a preamplifier in the sensor and then to the main particle counter. Each particle passing the window interrupts a portion of the light beam according to its size and causes a momentary reduction in the phototube output signal. The counter measures the maximum area of the particle exposed as it passes through the measuring zone.

HIAC particle counter is capable of sizing particles in liquids or gases up to 12 size ranges simultaneously, these ranges can be preset according to calibration curve which is generated by running a suspension containing mono-sized spherical particles having accurately known diameters through the sensor.

7. Colloid Titration

Most filtration plants still rely on the jar test for coagulant dosage control. Dosage control through the means of zeta potential measurement has not been used extensively, mainly because of the difficulties encountered in the measurement procedure. Colloid titration technique is an alternative to either zeta potential measurement or the jar test procedure for the measurement of charge characteristics of colloids, determination of the isoelectric point of the system, and for the determination of effective polymer dosage. This technique is based on the fact that a positive colloid reacts stoichiometrically with a negative colloid forming a precipitate at the isoelectric point. A positive colloid can be titrated directly by PVSK (potassium polyvinylsulfate) solution with toluidine blue (TB) as the indicator. For negative colloid, a known excess amount of positive colloid must be added to the negative colloid suspension. The oppositely charged colloids react very nearly stoichiometrically and are neutralized. Then the remaining excess positive colloid is back titrated by PVSK. In this titration the positive colloid used was glycol chitosan (GC).

The reaction of PVSK with GC in the presence of TB is shown below



The indicator TB maintains its blue color in the presence of positive colloids. However, it turns purple when it is adsorbed on a negative colloid.

Many polymers exhibit a considerable variation in surface charge density as the pH is varied. The charge density of PDADMA (Cat-Floc) does not change in the pH range of interest in water treatment. This was used to determine the charge density of the bentonite (Fisher Scientific Co., Fairlawn, NJ) suspension used throughout this study.

8. Refiltration Technique

According to Carman-Kozeny's permeability theory, the filtration rates of liquid through filter cakes are related to the surface areas of the solids in the cakes. When the pressure drops across the sludge cake, the thickness and cross-sectional area of the cake, and the porosity of the bed are kept constant, the volume rate of flow of filtrate is inversely proportional to the square of the effective particle surface area in a unit volume of filter cake. In order to measure the filtration rate through a filter cake of constant and known thickness, the first filtrate is passed through the cake obtained from the initial filtration in which the solid is still settling during the process.

In this study, the procedure was as follows: After the bentonite suspension was mixed with a definite dosage of a polymer for a certain period of time, 100 ml aliquot was filtered under a 15 inch mercury vacuum through a membrane filter having a diameter of 47 mm and an average pore size of 0.45 μ . The filtrate was collected and refiltered through the cake under identical conditions.

The time required to collect 10 and 35 ml of filtrate during the refiltration step was noted and the difference designated as the refiltration time.

9. Laboratory Filtration Studies

A constant rate direct filtration pilot unit was used for this step. The filtration system, as shown in Figure 2, consists of four components: an influent preparation and feed system, a polymer feed system including polymer pump and ~~pretreatment mixing chamber with arrangement for controlling mixing intensity~~ and time of mixing, G and t , respectively, and a filter column and flow rate control assembly.

The polymer mixing chamber could be fitted with either a one or a four blade impeller to study different ranges of velocity gradient, G . The reaction volume was 3.7 liters. However, this could be controlled to lower values simply by wasting a fraction of the feed flow into the mixing chamber. The impeller was provided with a shaft-mounted torquemeter to measure the torque input accurately and to estimate G from Figure 1. The mixing time in the reactor could be varied from 3.5 to 25 minutes by varying the flow rate through the filtration system from 3.5 to 0.5 gpm/sf, respectively.

As the present filtration study focuses on the effect of chemical pretreatment by various polymers, the filter runs had to be continued until deterioration in effluent quality was detected. Adin et al. (38) suggested using a single medium of sand with a small depth, perhaps 15 to 20 cm, to study the effect of chemical pretreatment on filtration. They elaborated that to achieve breakthrough, a reduction in filter depth is preferred over excessive alteration in grain size or filtration velocity. Since the primary objective of this study was to evaluate alternative chemical treatments, it is better to keep the physical transport mechanisms constant and within their known range of effectiveness. Any

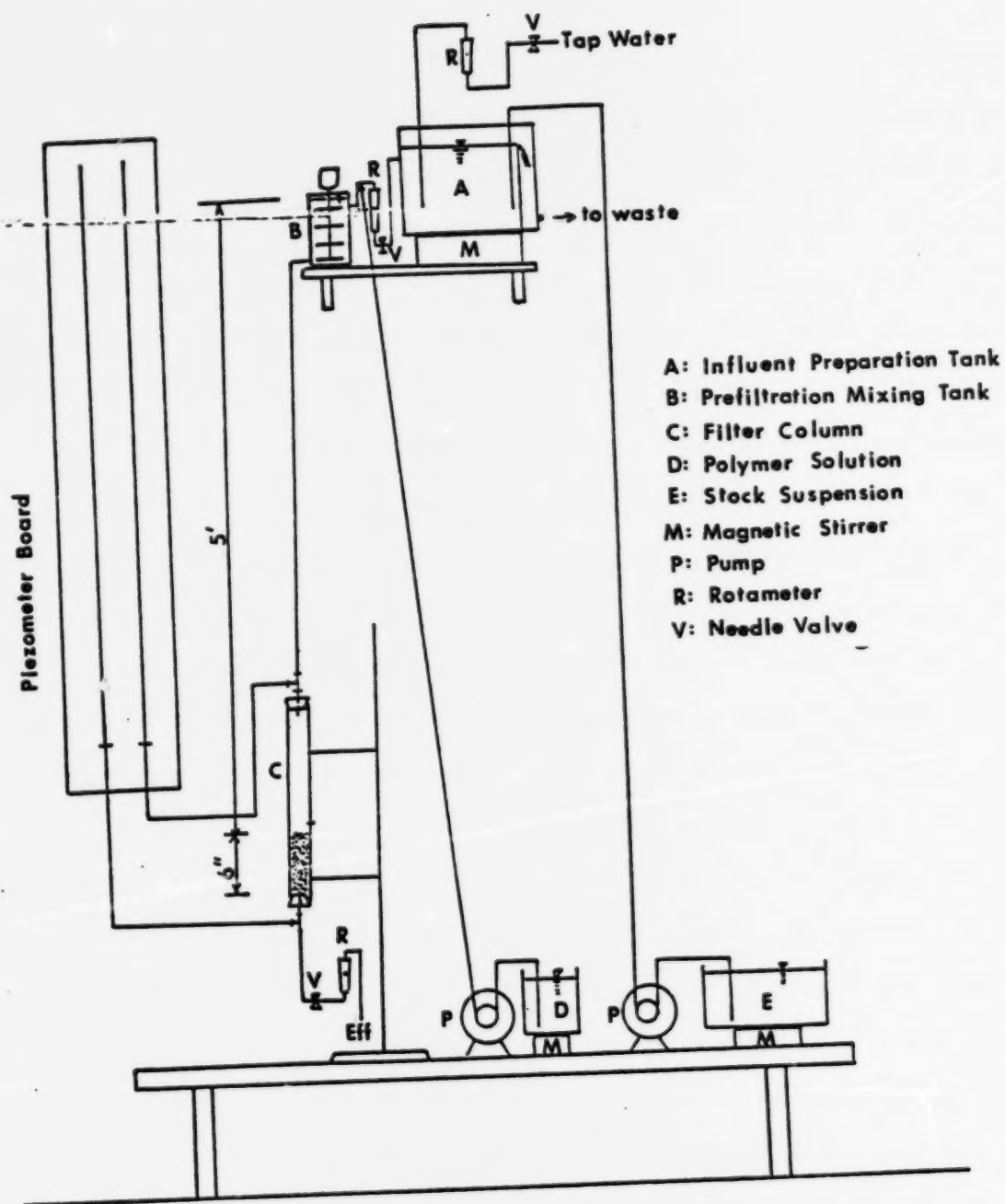


Fig. 2. Schematic Diagram of the Direct Filtration System

difference in filtrate quality observed when using different chemical pretreatments can then be attributed to destabilization and attachment effectiveness rather than to transport mechanisms. A shallow filter depth also has the advantage of being able to get the complete breakthrough curve within a short time, but permitting prediction of filter performance to be expected with greater depths.

In this study, a small filter column with 1-in. ID plexiglass and 6-in. depth of silica sand (effective size 1.0 mm, uniformity coefficient 1.2) was used. For all filter runs an influent turbidity of 20 NTU was obtained by suspending 75 mg/l of bentonite clay in the University tap water. The pretreatment, type and dose of polymer, and mixing intensity and mixing time, were the control variables. During a filter run, the turbidity, particle size distribution, and headloss were recorded. The rate of filtration was varied from 2 to 3.5 gpm/sf.

In certain experiments, a dual media filter column, consisting of 20 inches of anthracite (effective size 0.7 mm, porosity 0.55, and uniformity coefficient 1.6) overlying 12 inches of sand (effective size 0.5 mm, porosity 0.42, and uniformity coefficient 1.52) was used. This filter column was 3-in. ID and had provisions for the collection of samples and measurement of headloss at different depths. The influent for these filter runs consisted of a mixed metal hydroxide suspension. The stock metal solution was prepared by adding 1.0 N NaOH slowly to the solution containing 1200 mg/l of nickel, 240 mg/l zinc, and 60 mg/l copper, until a pH of 10.5 was reached. Appropriate dilutions of stock suspension were made to obtain the desired influent turbidities. The pH of the influent was about 8.5. Typically, samples were collected at depths of 11.5 in. (anthracite layer), 19.5 in. (anthracite-sand interface), 25.5 in. (sand layer), and 31.5 in. (filter effluent). The samples were analyzed for turbidity, size

distribution, and metals. The dual media filter was backwashed at the end of each filter run when a predesignated effluent turbidity and/or headloss were exceeded. However, for the single media sand filter, fresh sand was used for each filter run.

Chapter 4

RESULTS AND DISCUSSION

A. Preliminary Screening Studies for Polymers

Initially, viscosity, conductivity and colorimetric measurements were made to determine if any of these measurements could be used in selecting polymers prior to using more sophisticated techniques, such as colloid titration, and electrophoretic mobility.

The data on viscosity for 0.2% solutions were recorded for several polymers. These polymers were used to remove turbidity from a bentonite suspension with an initial turbidity in the range of 50-77 NTU. The fractional turbidity remaining following 2 minutes of rapid mixing (100 rpm), 20 minutes flocculation (20 rpm) in a standard Phipps-Bird jar test apparatus, and 30 minutes settling, using optimum dosages of various polymers are shown along with their viscosities in Table 2. The more viscous polymers with high molecular weights should have exhibited lower final turbidities. This was not apparent. The measurement of viscosity was done with less than desirable precision. A better instrumentation was needed to measure such low viscosities.

One of the major mechanisms in flocculation is destabilization of the electrically charged particles, allowing them to agglomerate and settle out. Electric conductivity of a colloidal suspension is inversely proportional to the colloidal electric potential. Therefore, conductivity of water should change by the addition of a polymer as a function of the colloidal zeta potential of the suspension, besides the usual change expected by the addition of an electrolyte. The results in Table 3 show that, as expected, the specific conductance increased as the cationic polymers were added. Although the data shows no definite relationship between conductance and turbidity removal, the best results were obtained when the conductance was in the range of 30 - 40 micromhos/cm.

Table 2

Relationship Between Viscosity and Turbidity Removal with Polymers

Polymer	Viscosity (centipoise)	Opt. dose of 0.2% solution (mg/l)	Initial Turbidity (C_0) (NTU)	Residual Turbidity (C/C_0)
Betz 1160	1462	125	65	0.352
Betz 1180	48	58	50	0.04
Betz 1190	66	16	60	0.042
Percol 757	2354	64	55	0.145
Percol 763	1340	110	77	0.052

Table 3
Relationship Between Conductance and
Turbidity Removal

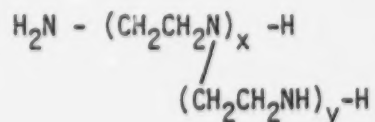
Polymer	Conc. (mg/l)	Conductance of Clay Soln. (micromhos/cm)	Conductance of Clay Soln. + Polymer (micromhos/cm)	Residual Turbidity (C/Co)*
Percol 757	64	26	36	0.145
Percol 763	64	38	38	0.234
Betz 1160	64	17	27	0.508
Betz 1180	64	16	36	0.04
Percol 757	32	26	31	0.182
Percol 763	32	38	52	0.442
Betz 1160	32	17	30	0.569
Betz 1180	32	16	26	0.38
Percol 757	16	26	27	0.582
Percol 763	16	38	70	0.532
Betz 1160	16	17	20	0.923
Betz 1180	16	16	20	0.9

*Initial turbidities are the same as shown in Table 2 for the various polymers

B. Colloid Titration of Polymers

Colloid titration techniques were employed to determine the charge characteristics of cationic polymers as a function of pH. Wherever possible, pH of zero point charge, pH_{ZPC} , was estimated from extrapolation. This method was also used to determine the charge density of bentonite clay. The titrant used in this study was a 2.5×10^{-3} M solution of potassium polyvinylsulfate (PVSK) standardized against 2.5×10^{-3} M standard solution of cetylpridinium chloride monohydrate solution using a 0.1% solution of toluidine blue (TB) as the indicator.

In order to determine the charge of cationic polymer solution, 10 ml of a 1 mg/ml polymer solution was diluted to about 50 ml using distilled water and titrated directly with PVSK with 2 drops of TB to an end point color change from blue to red-violet. pH adjustment of polymer solutions were made with either 0.1 N H_2SO_4 or 0.1 N NaOH . Typical results for charge distribution of certain polymers are shown in Figures 3 - 5. Polyethylinimine polymers (Fig. 4) show a significant variation in charge density depending on the pH. The basic composition of PEI is as below



Betz polymer 1160 (acrylamide copolymer) also showed a charge density dependence on pH whereas 1180 and 1190 (polyamides) showed a very weak charge density dependence, if any, on pH as shown in Fig. 3. Polydiallyldimethylammonium (PDADMA), commonly known as Cat-Floc, does not exhibit any charge dependence on pH as shown in Fig. 5, which also shows charge density variation of Percol 751 (acrylamide based), polymer.

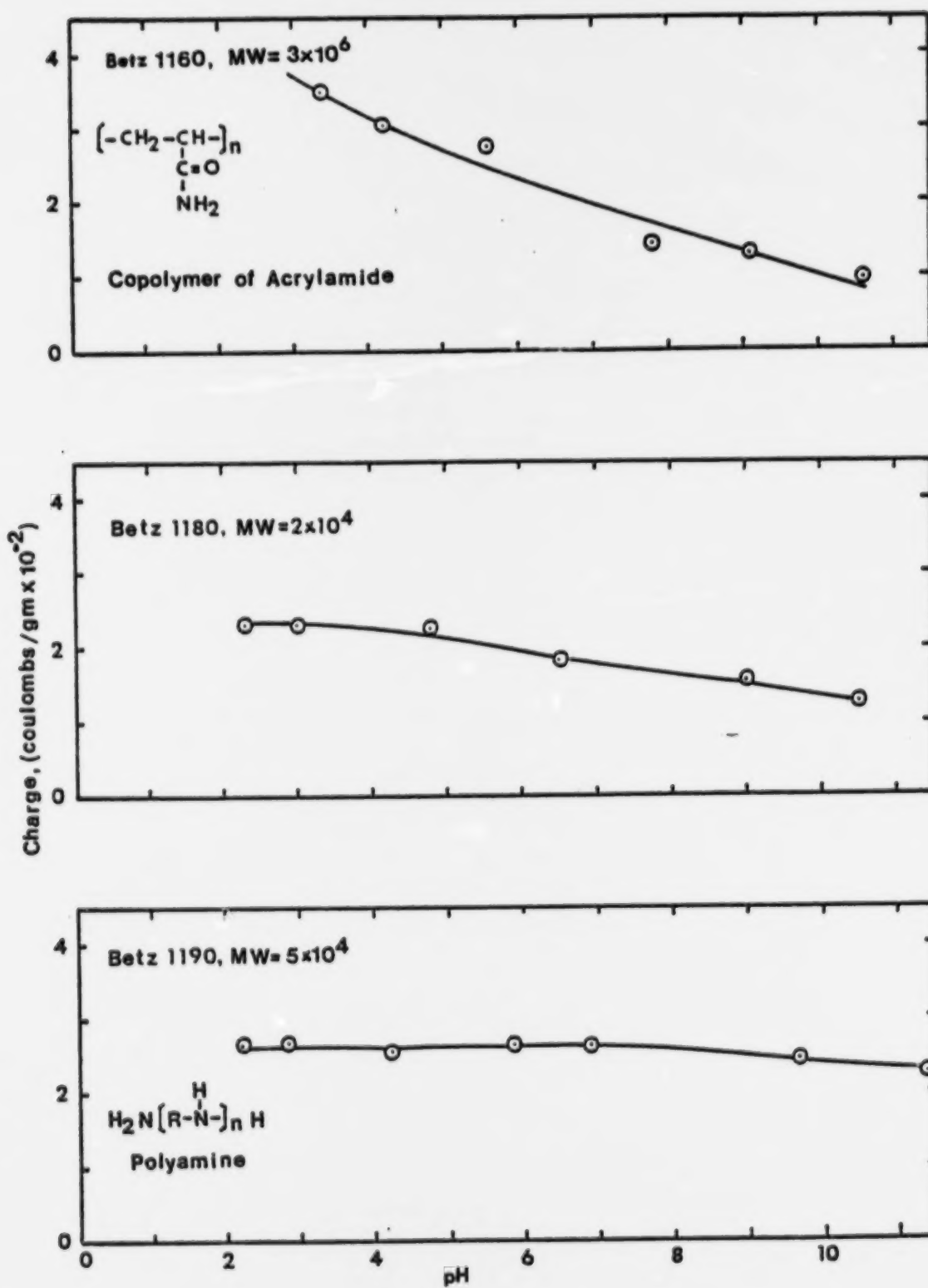


Fig. 3. Charge Density of Betz Polymers

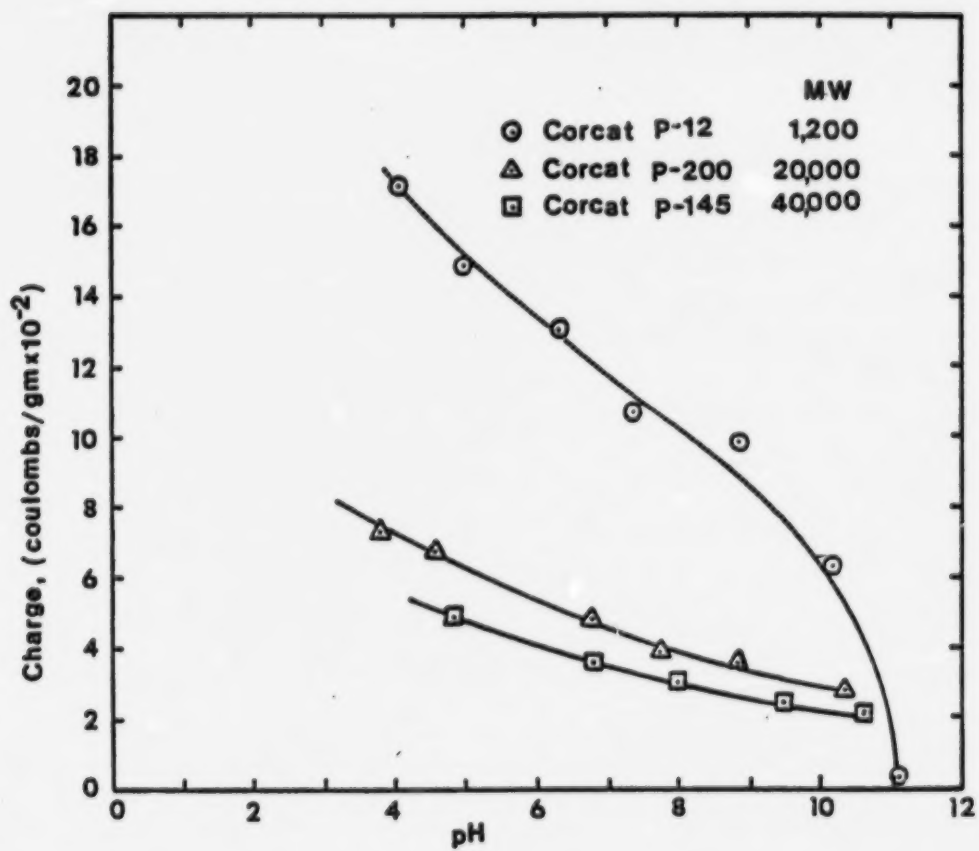


Fig. 4. Charge Density of Polyethylenimines

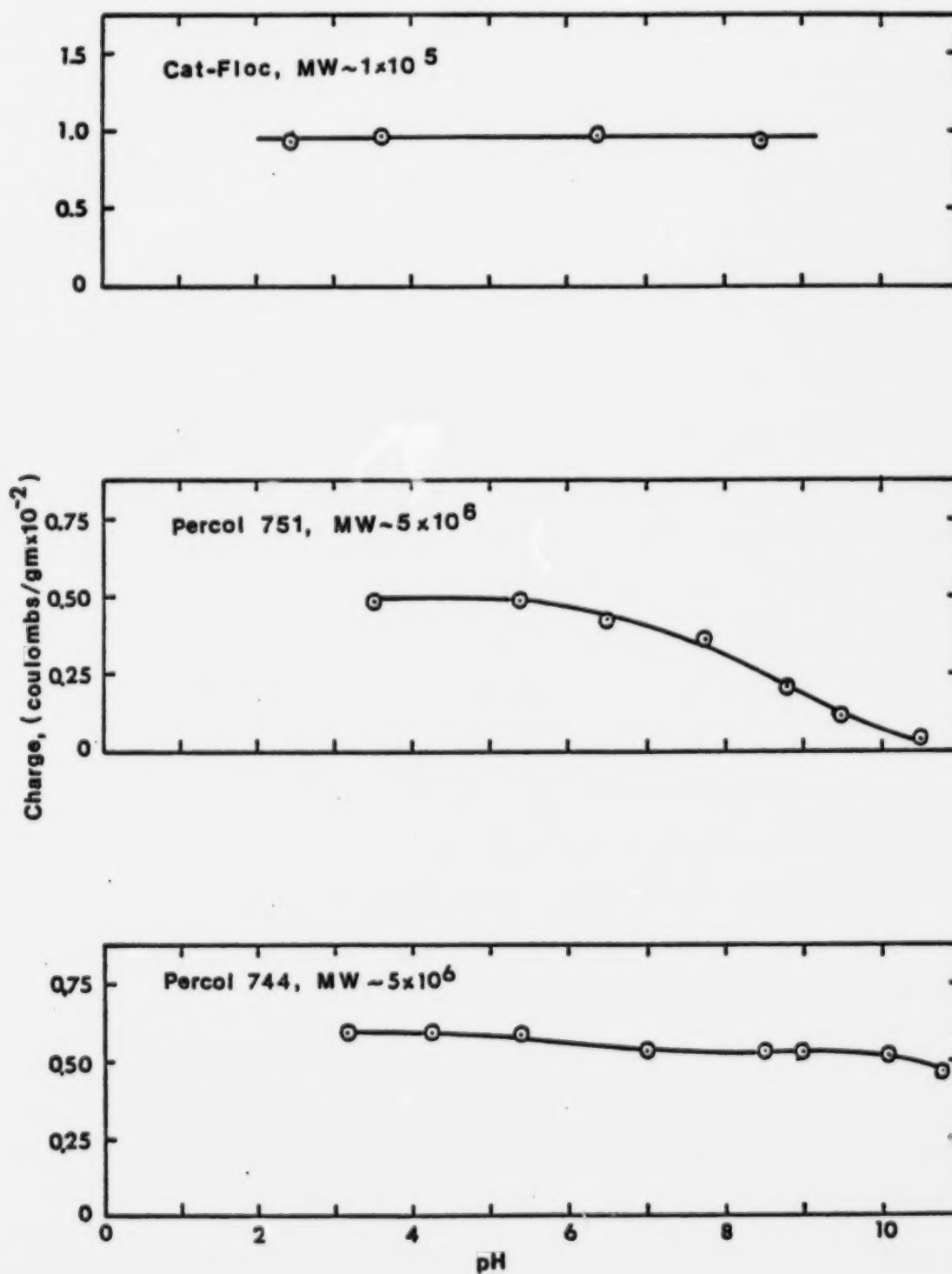


Fig. 5. Charge Density of Acrylamide Base (Percol) Polymers and PDADMA (Cat-Floc)

In order to determine the charge density of bentonite (Fisher Chemical Co.) clay, 5 ml of a stock bentonite suspension (100 mg/l) was diluted 10-fold with distilled water to a volume of 50 ml to which 3 ml of a stock Cat-Floc solution (1 mg/ml) were added along with 2 drops of TB indicator. The excess cationic charge was titrated with the standard PVSK titrant solution using a 2 ml microburette to an end point of light blue to bluish purple. The charge density per gram of clay could then be calculated from the titration results. The exchangeable anions in 5 ml of a 100 mg/l bentonite suspension were equivalent to 0.16 ml of 2.05×10^{-3} N PVSK solution. From this, the cation exchange capacity (CEC) of bentonite was calculated to be 0.656 mg/gm which is equivalent to $(0.656 \times 10^{-3}) \times (6.01 \times 10^{23}) = 3.95 \times 10^{20}$ monovalent cation per gm. The corresponding charge density of bentonite was $.656 \times 96.5 = 63.3$ coulombs/gm. From available data in the literature the surface area of bentonite, based on a unit cell weight of about 900, was estimated to be 803 m²/gm. Therefore, the charge density was 7.88 microcoulombs per sq cm. Table 4 summarizes the results for charge density and electrophoretic mobility of certain selected polymers used in this study. For most experimental filter runs and coagulation experiments, the university tap water was used. This water has a pH in the range of 7.8 to 8.2 and an alkalinity of 300 mg/l as CaCO₃. The ionic strength of the water is estimated to be 4.5×10^{-3} M. In classifying the polymers, an average charge density has been reported for those polymers not exhibiting a marked variation of charge with pH. All mobility and zeta potential measurements were made at a room temperature of $25 \pm 2^\circ\text{C}$.

C. Electrokinetic Measurements

When a colloidal suspension is subjected to an electrical field, the individual particles will migrate to the electrodes. The direction and velocity of migration depends on the nature and the amount of charge on the colloid and the strength of the applied field. Electrophoretic mobility and zeta potential, the two most commonly used measurements for electrokinetic behavior of charged

Table 4

Charge Characteristics of Cationic Polymers

Polymer	Manufacturer	Charge (coul/gm)		Optimum pH	Zeta Potential		
		Soln. pH	Charge at pH		Soln. pH	E.M.	Z.P.
Betz 1180	Betz	3.0	230				
		5.0	210				
		9.0	152				
Betz 1160		3.4	350				
		5.0	270				
		9.0	130				
Betz 1190		---	---	260	3-8		
Betz 1250		4.2	29.0		4.0	1.43	+18.8
		7.2	9.7				
		9.9	55.0				
Corcat P-12	Cordoba Chem.	4.1	1720				
		9.0	850				
		11.1	30				
Corcat P-145		5.0	480				
		8.0	300				
		10.6	200				
Cat-Floc	Calgon	---	---	92	3-10		

E.M. - Electrophoretic Mobility, $\frac{\text{microns/sec}}{\text{volt/cm}}$

Z.P. - Zeta Potential, Millivolts

particles, measure the extent of repulsive forces acting on the particles. Zeta-Meter (a product of Zeta-Meter, Inc.) was employed for all electrokinetic measurements.

Typical results for the electrophoretic mobilities of a 75 mg/l bentonite suspension, with an initial turbidity of 20 NTU, are shown in Figures 6 through 9, as a function of dosages of seven cationic polymers. All experiments were conducted at a pH of 8.0 and using tap water with an ionic strength of $4.5 \times 10^{-3}M$. The dosages of PEI series polymers, Corcat P-12 ($\langle M \rangle_n = 1200$) and Corcat P-145 ($\langle M \rangle_n = 40,000$), showed some difference in dosages for obtaining an electrophoretic mobility of zero, that is, zero zeta potential, for the same bentonite suspension, as shown in Figure 6. The difference in dosage could possibly be ascribed to either difference in molecular weight or charge density of these two polymers. Further analysis of this data has been presented elsewhere in this report. The dosages obtained with Percol 744 and 751, both with a number average molecular weight, $\langle M \rangle_n$, of 5×10^6 , and similar charge densities, approximately 50 coulombs/gm at pH 8 (Fig. 5), for neutralizing the net negative charge on the 20 NTU bentonite suspension are very similar. Typical data for Cat-Floc ($\langle M \rangle_n = 1 \times 10^5$, charge = 92 coul/gm), Betz 1160 ($\langle M \rangle_n = 3 \times 10^6$, charge = 146 coul/gm) are shown in Figure 8 and 9, respectively. It should be noted that in all experiments in this series, the polymer was mixed with bentonite suspension for 3 minutes using a magnetic stirrer prior to actual measurements of mobility.

D. Jar Tests

In order to determine the optimum dosage for turbidity removal by coagulation-flocculation and by direct filtration, jar test is the most commonly used laboratory procedure. The correspondence between the dosages for optimum coagulation and for direct filtration has been reported recently (22) (33). In this research, jar tests were used to determine the optimal dosage for floc-

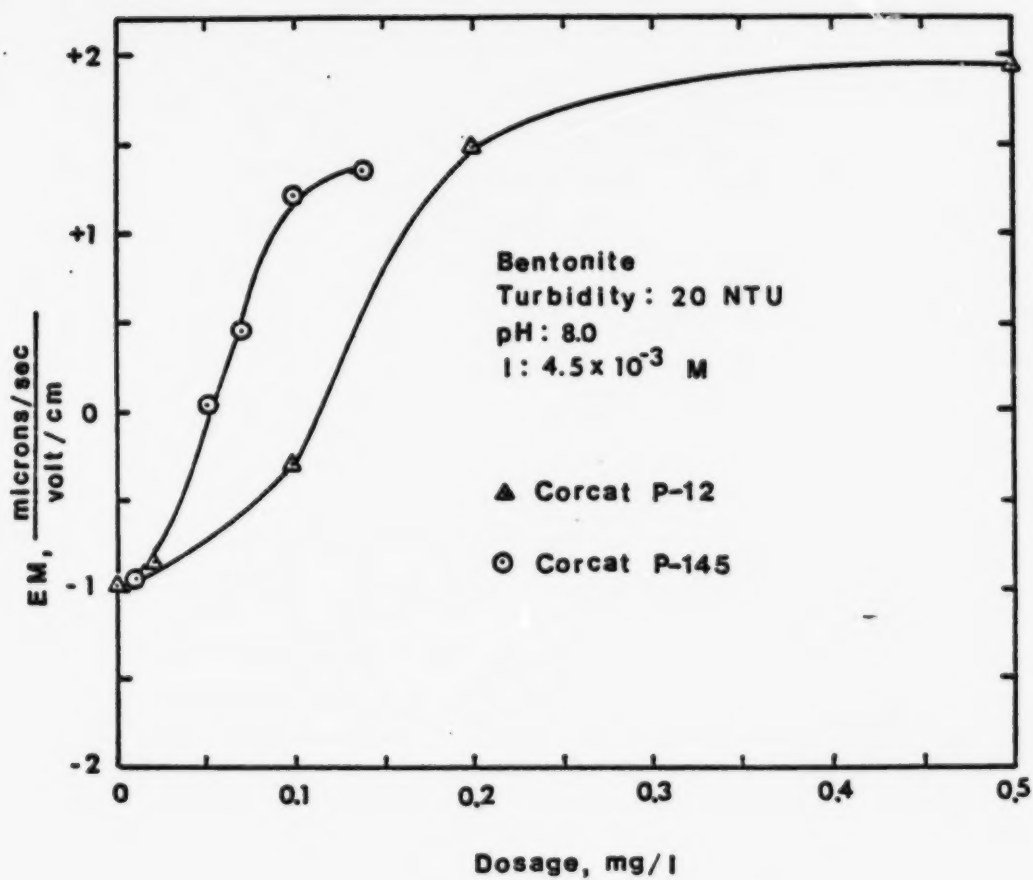


Fig. 6. Electrophoretic Mobility of Bentonite at Various Dosages of PEI Polymers

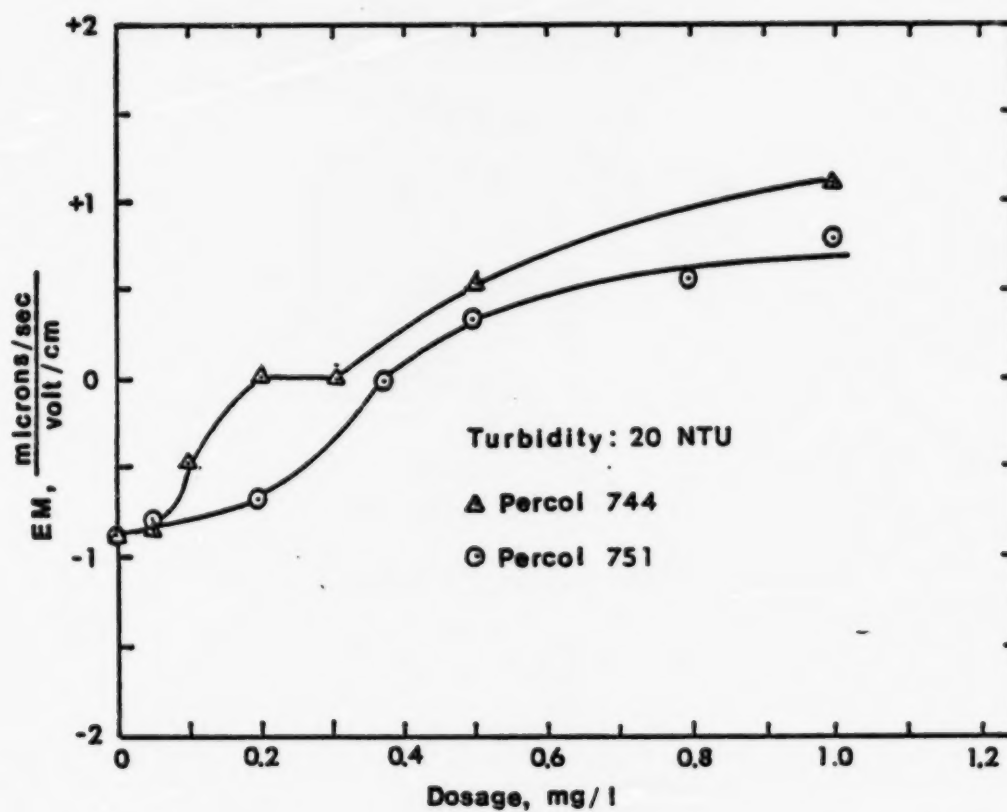


Fig. 7. Electrophoretic Mobility of Bentonite at Various Dosages of Percol Series Polymers

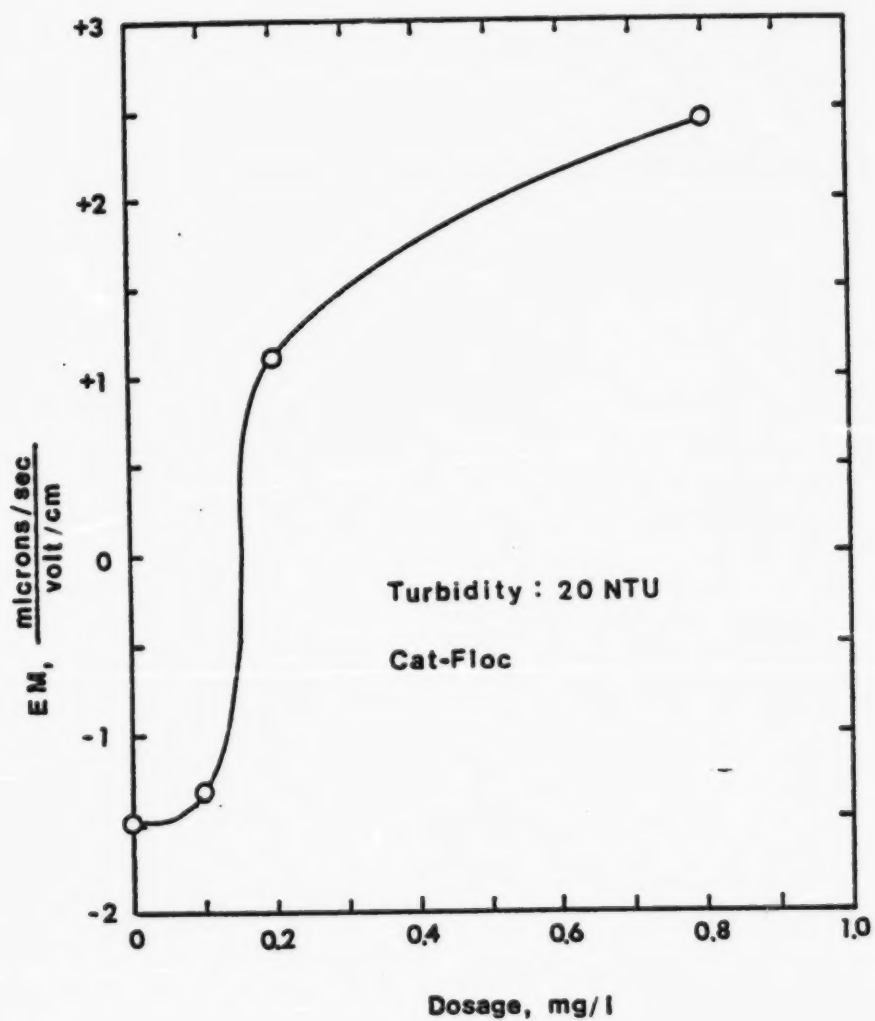


Fig. 8. Electrophoretic Mobility of Bentonite at Various Dosages of Cat-Floc (PDADMA)

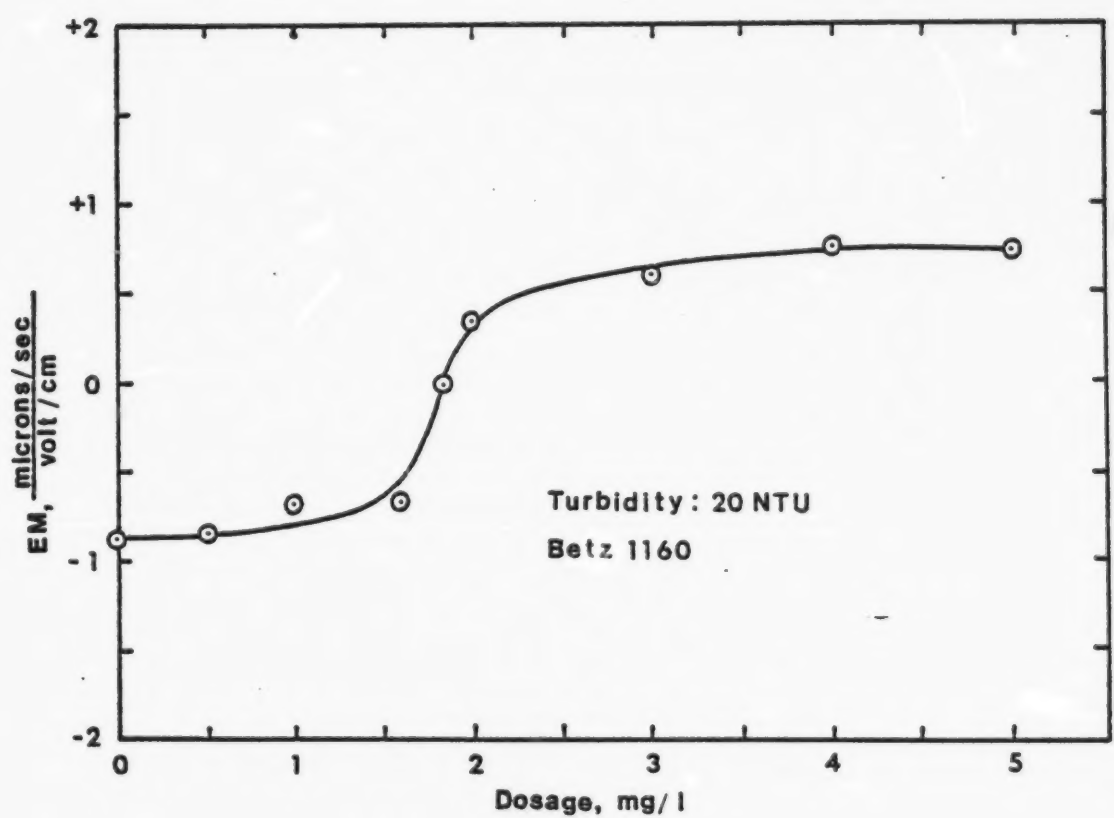


Fig. 9. Electrophoretic Mobility of Bentonite at Various Dosages of Betz 1160

culatation of simulated turbid water using given cationic polymers. The effect of turbulence during polymer mixing and, subsequently, the period of flocculation, on the optimal polymer dosage, both for flocculation and direct filtration were also investigated.

Figure 10 shows the results of jar tests for two polymers, namely Cat-Floc and Betz 1190. A 40 NTU bentonite suspension was used. The turbid water was prepared by suspending 150 mg/l of bentonite per liter of university tapwater the composition of which has been given elsewhere. The polymers were mixed for one minute at a paddle speed of 85 rpm ($G=200 \text{ sec}^{-1}$) in a standard Phipps and Bird jar test apparatus, followed by 25 minutes of slow agitation at a paddle speed of 25 rpm ($G=40 \text{ sec}^{-1}$). A further 30 minutes of quiescent settling was permitted prior to withdrawing a supernatant sample of the test suspensions for residual turbidity measurements using a Hack 2100A turbidimeter. For both Betz 1190 and Cat-Floc, with dissimilar molecular weights, the optimum dosage appeared to be very similar. Figure 11 shows the results of jar tests for bentonite suspensions with initial turbidities of 20 and 40 NTU using a cationic polymer, Betz 1175 ($\langle M \rangle_n = 1 \times 10^4$). Apparently, a weak stoichiometry between colloid surface concentration and polymer dosage was indicated. The optimum dosage of Betz 1175 for initial turbidities of 20 and 40 NTU were 1.13 and 2.6 mg/l, respectively.

E. Correlation Between Jar Test and Electrokinetic Measurements

The correlation between electrophoretic mobility and optimum dosage of a cationic polymer, Corcat P-145 (polyethylenimine; $\langle M \rangle_n = 4 \times 10^4$), in the flocculation a 20 NTU suspension of bentonite is presented in Figure 12. The optimum dosage of 0.05 mg/l corresponds extremely well with an electrophoretic mobility of zero as shown in Part A of Figure 12. In part B of this figure, the ratio of charges of bentonite to the polymer at various dosages has been plotted

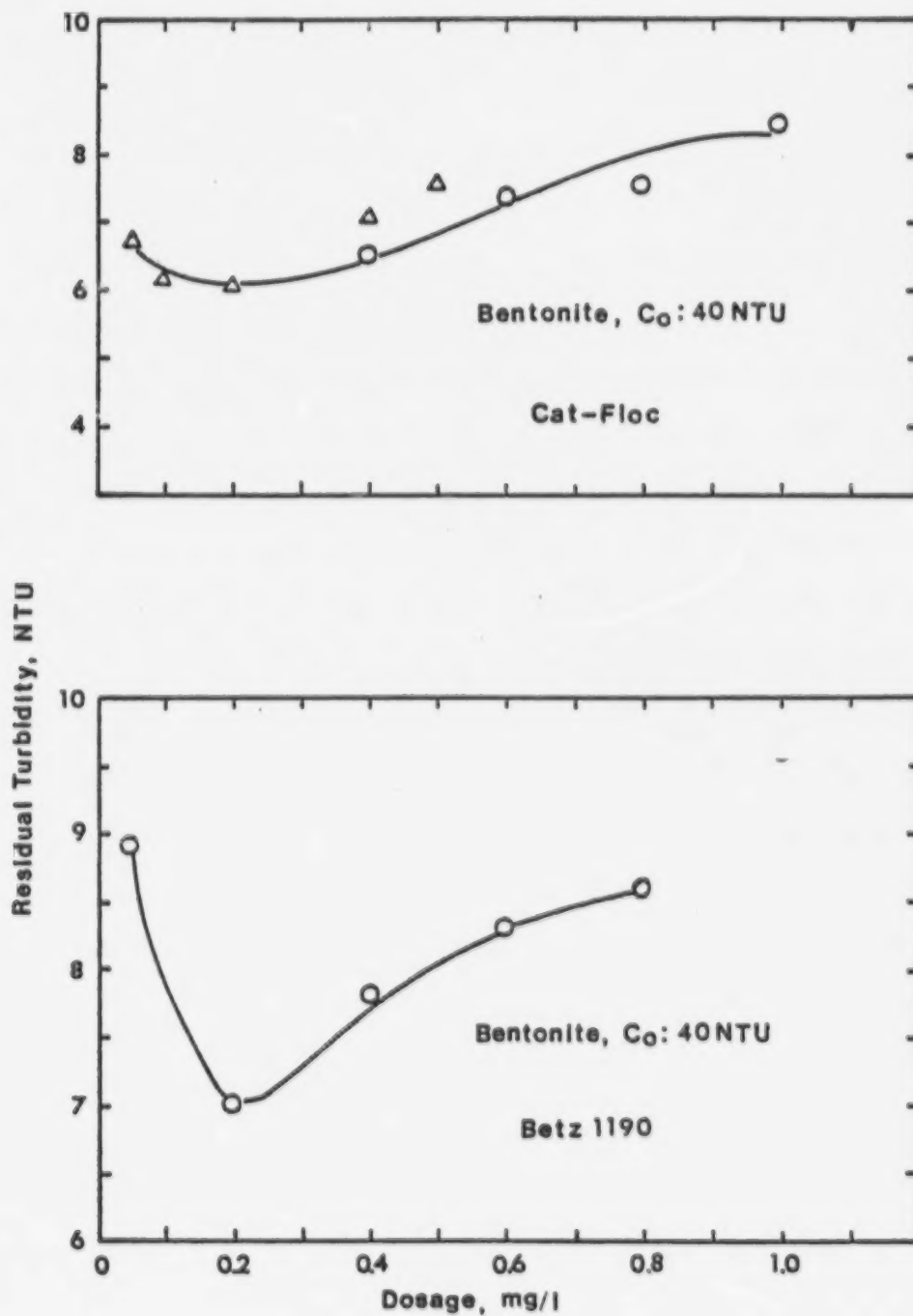


Fig. 10. Residual Turbidity from Jar Tests for Cat-Floc and Betz 1190

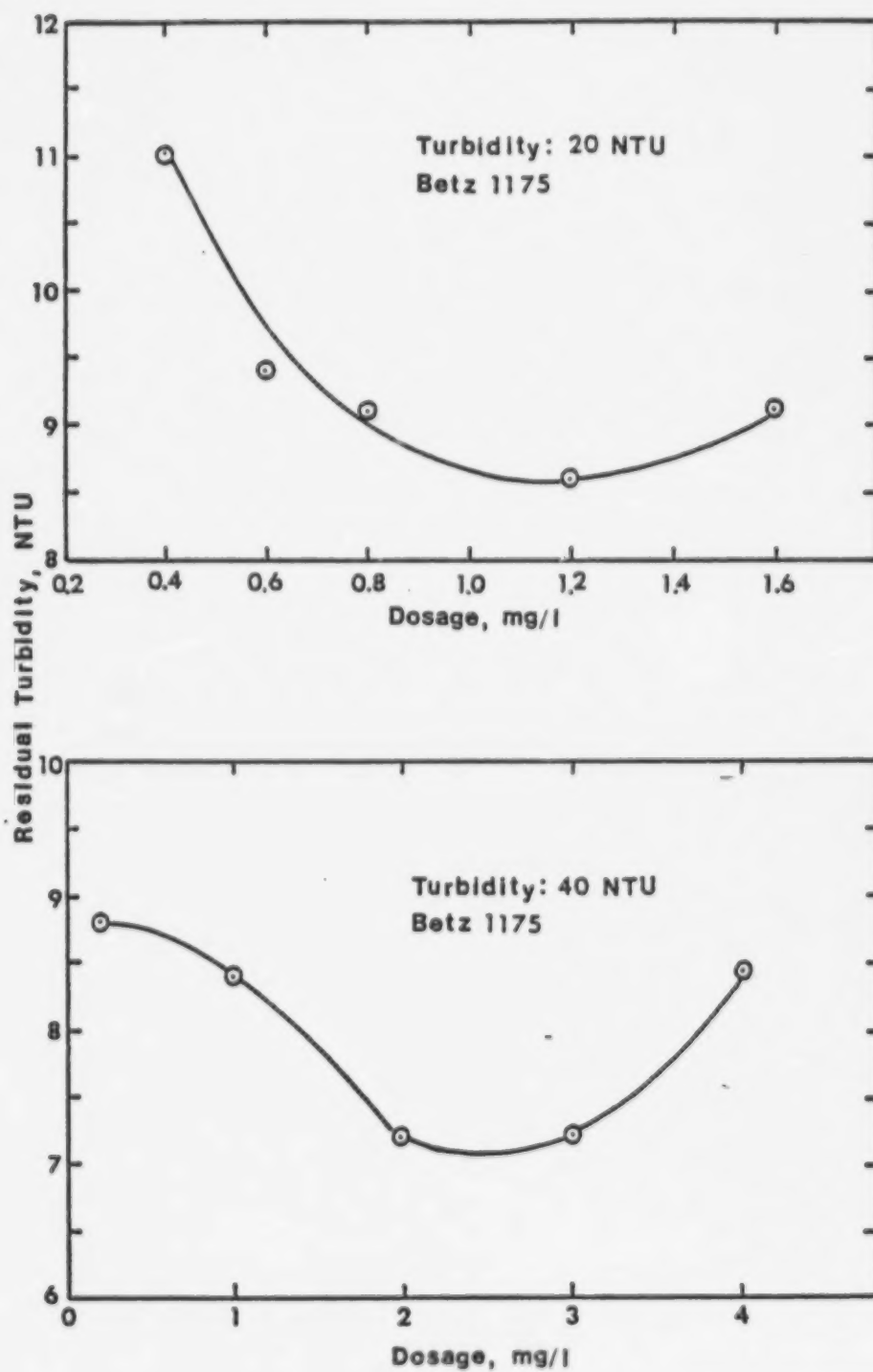


Fig. 11. Stoichiometry in Flocculation with Betz 1175

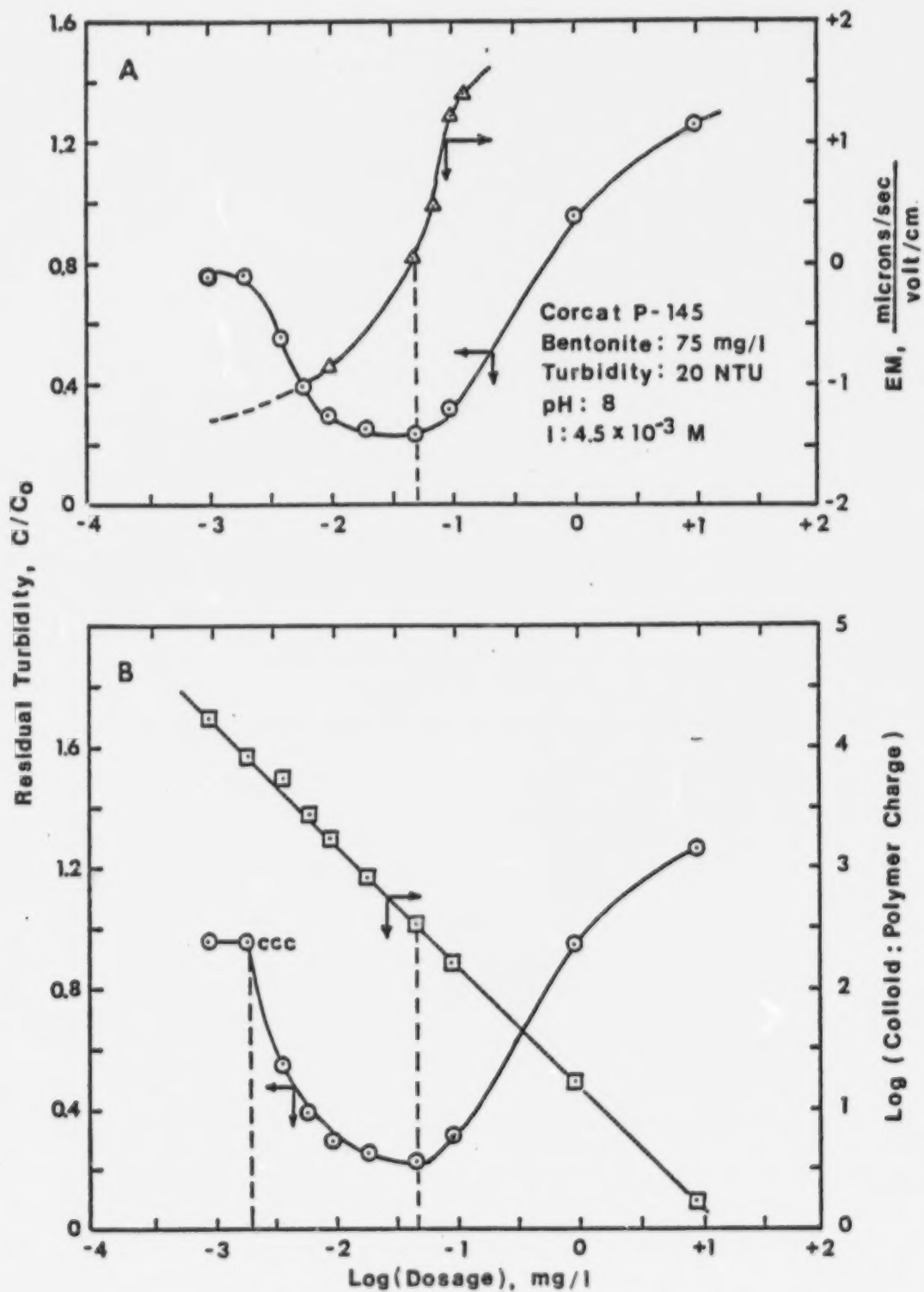


Fig. 12. Relationship Between Electrophoretic Mobility and Polymer Dosage (Corcat P-145)

on logarithmic scales. The residual turbidity versus log of polymer dosage is also replotted for the purpose of comparison. Table 5 shows the details of these stoichiometric calculations for both Corcat P-145 and Corcat P-12. There was no one to one charge neutralization observed at the optimum dosage. The ratio of colloid to polymer charge was extremely high at optimum dosage. Therefore, although charge neutralization appears to be a major mechanism of flocculation with low molecular weight cationic polymers as seen in Figure 12A, there is no linear stoichiometry between polymer and colloid charges (Figure 12B) indicating bridging to be responsible, in part, for the observed results. The fact that logarithm of colloid-to-polymer charge ratio bears a linear relationship with logarithm of polymer dosage is no coincidence since the colloid charge in this experiment was a constant while polymer charge was varied. The ratio of colloid-to-polymer charges at the critical coagulation concentration (CCC) of 2.51×10^{-3} mg/l is 5650 and that at the optimum dosage of 0.05 mg/l is 339. Figure 13 shows similar results for another polyethylenimine series polymer, Corcat P-12 ($\langle M \rangle_n = 1200$), used to coagulate the same bentonite suspension at pH 8.0. As in the case of Corcat P-145, the correspondence between optimum polymer dosage (0.1 mg/l) and zero electrophoretic mobility was excellent although there was no one to one correspondence between the polymer charge and colloid charge. Figure 14 presents results from jar tests for yet another polyethylenimine series polymer, namely, Corcat P-200 with a number-average molecular weight of 20,000 and a charge density of 380 coulombs/gm at a pH of 8 at which the experiment was conducted.

Results of jar tests have been compared with electrokinetic data for other polymers, namely, Percol 751, and Betz 1160 in Figures 15 and 16. Again, all of the studies were done with an identical 20 NTU bentonite suspension as reported previously. For Percol 751, the CCC and optimum dosages were 0.014 and 0.316 mg/l, respectively. The agreement between optimum dosage and zero

Table 5
Stoichiometry Between Polymer and Colloid Charges
for 20 NTU Bentonite Suspension at pH 8

Corcat P-145			Corcat P-12		
Dose (mg/l)	Charge (coul/l)	Colloid* Polymer	Dose (mg/l)	Charge (coul/l)	Colloid* Polymer
.001	3×10^{-4}	1.58×10^4	.001	.001	4.75×10^3
.002	6×10^{-4}	7.92×10^3	.01	.01	4.75×10^2
.003	9×10^{-4}	5.28×10^3	.04	.04	1.19×10^2
.006	1.8×10^{-3}	2.64×10^3	.06	.06	79.2
.01	3×10^{-3}	1.58×10^3	.08	.08	59.4
.02	6×10^{-3}	7.9×10^2	0.10	0.1	47.5
.05	1.5×10^{-2}	3.17×10^2	0.3	0.3	15.8
.10	3×10^{-2}	1.58×10^2	0.5	0.5	9.5
1.0	3×10^{-1}	1.58×10	1.0	1.0	4.75
10.0	3.0	1.58	10.0	10.0	.48

*Ratio of charge calculated based on a bentonite concentration 75 mg/l (20 NTU). The charge concentration of bentonite suspension at pH 8 is 4.75 cou/l. The charge densities of corcat P-145 and P-12 at pH 8 are 0.3 and 1.0 coul/mg, respectively.

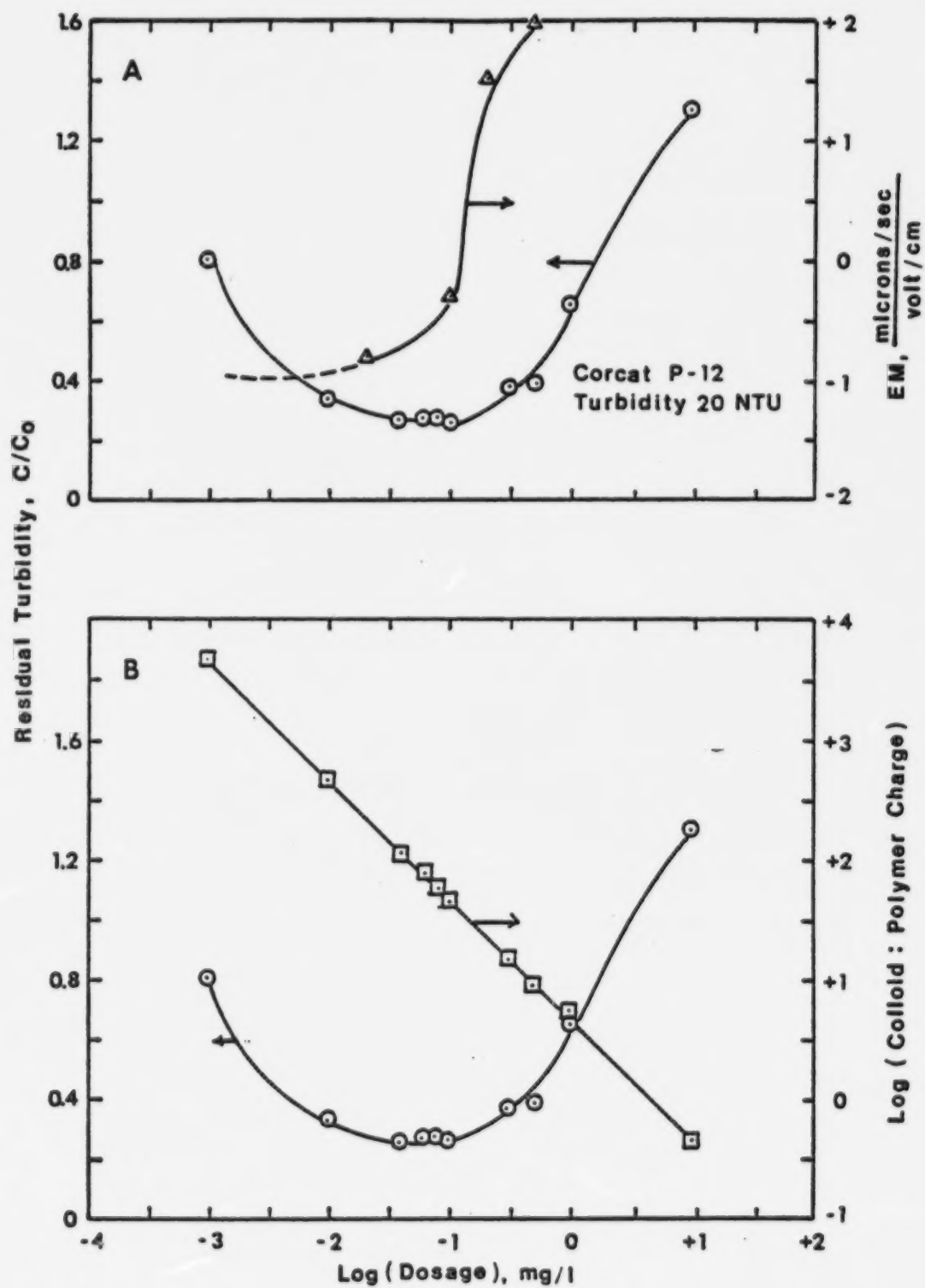


Fig. 13. Relationship Between Electrophoretic Mobility and Polymer Dosage (Corcat P-12)

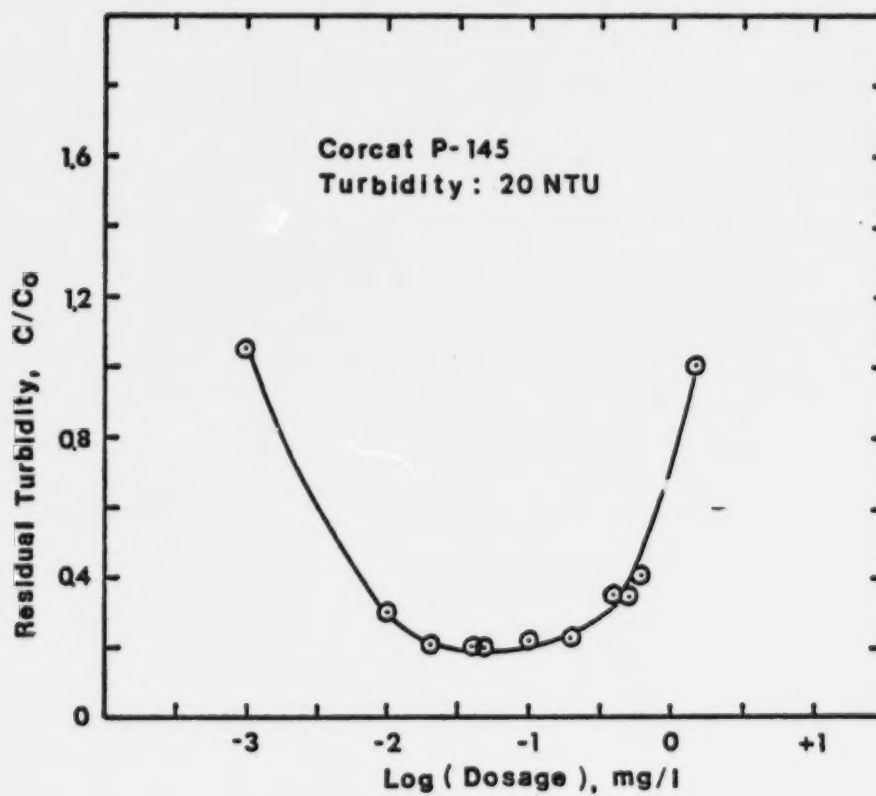


Fig. 14. Turbidity Removal with Corcat P-200

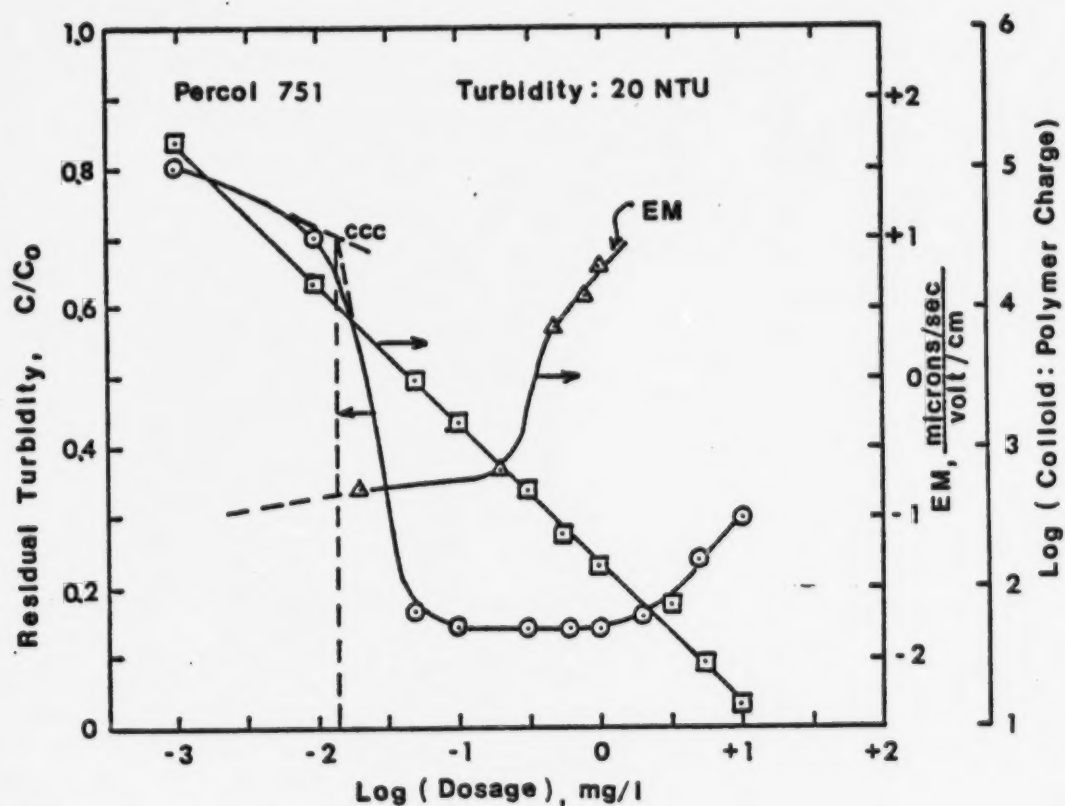


Fig. 15. Relationship Between Electrophoretic Mobility and Polymer Dosage (Percol 751)

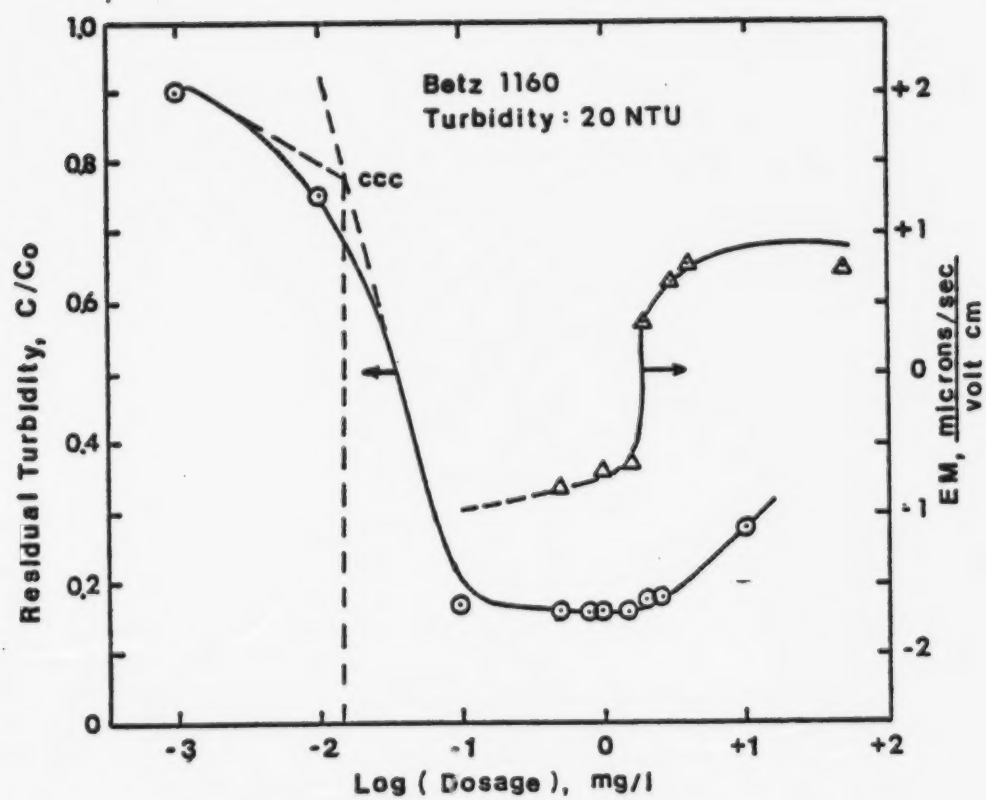


Fig. 16 Relationship Between Electrophoretic Mobility and Polymer Dosage (Betz 1160)

electrophoretic mobility (EM) was excellent. From a charge neutralization standpoint, no stoichiometry between positive and negative charges was obtained, since the optimum point did not correspond to a colloid-to-polymer charge ratio of unity. Figure 16 shows that CCC and optimum dosages for Betz 1160 were 0.016 and 0.2 mg/l, respectively. Table 6 summarizes results of jar tests and electrokinetic studies using 20 NTU benotnite suspension at pH 8.

F. Effect of Velocity Gradient on Polymer Dose, Floc Size and Floc Strength

The velocity gradient G plays a significant role in polymer-aided flocculation. As reported by many researchers, a high G must be maintained for a short time, usually no more than 3 minutes, to ensure uniform distribution and adsorption of polymers on colloidal particles. This should be followed by slow agitation, typically at a G of 10 to 75 sec^{-1} , to promote the growth of flocs. Finally, a quiescent settling period is provided to maximize solid-liquid separation. A convenient method of selecting polymers for direct filtration is by doing jar tests with the assumption that both coagulation and filtration processes are identical from a mechanistic standpoint. However, the slow mixing period, usually provided in the flocculation process, is not needed in filtration since the growth of flocs via the velocity gradient mode takes place within the filter voids. The determination of optimum dosage using jar tests considers both contact opportunity in flocculation and separation of phases. It is conceivable, therefore, that polymer mixing intensity may significantly alter optimum dosage and also the strength of floc formed within the filter bed. It is commonly believed that as the headloss in a clogging filter increases, the increased shear energy causes erosion of predeposited flocs from the media grains. Therefore, the effect of velocity gradient on the size and strength of floc were investigated. In all experiments of flocculation, size and size distribution of the flocs were measured. Optimum dosage was

Table 6
Summary of Jar Tests for 75 mg/l Bentonite
Suspension (20 NTU) at pH 8

Polymer	Charge Density (coul/gm)	ccc (mg/l)	Opt. dose (mg/l)	Colloid/Polymer Charge Ratio	
				ccc	Optimum
Corcat P-12 $\langle M \rangle_n = 1200$	1000	$\sim .001$	0.1	4750	48
Corcat P-200 $\langle M \rangle_n = 20,000$	380	$\sim .001$	0.02	12,500	625
Corcat P-145 $\langle M \rangle_n = 40,000$	300	$\sim .003$	0.05	5,280	317
Percol 751 $\langle M \rangle_n \sim 5 \times 10^6$	32.5	.014	.32	10,400	457
Percol 744 $\langle M \rangle_n \sim 5 \times 10^6$	51	.006	0.1	15,520	931
Betz 1160 $\langle M \rangle_n \sim 3 \times 10^6$	160	0.016	0.2	1,855	148

defined as that concentration of polymer which produced the largest mean size of flocs.

1. Effect of Rapid Mix Time

In order to determine the effect of time of initial rapid mix on floc size, flocculation experiments were conducted with 75 mg/l bentonite suspension. The polymers used were Betz 1190 and Corcat P-145 with molecular weights of 50,000 and 40,000 respectively. The dosage used for both polymers was 0.5 mg/l, somewhat higher than optimum. The value of 650 sec^{-1} for the rapid-mix velocity gradient was found to be optimum for these polymers. Figure 17 shows the results where the change in particle size for various number fractions has been plotted against time. Specifically, the size of particles finer than 90, 70 and 50 percent by count have been presented. For Betz 1190, the actual flocculation was complete within the first 4 minutes. Further flocculation at this G did not improve floc size. For Corcat P-145, the optimum mixing time appeared to be 8 minutes beyond which there was some break up of flocs. The stable floc size, that is, the size which did not change with time, appeared to be 15 microns, the 50 percentile size. In all subsequent experiments with polymers, the rapid mix time was limited to 3-8 minutes.

2. Effect of G on Floc Size Distribution and Optimum Polymer Dosage

Typical floc size distributions at various polymer dosages following 3 minutes rapid mixing at a G of 650 sec^{-1} are presented in Figures 18 and 19 for polymers Corcat P-12 and Betz 1160, respectively. No slow mixing was done before analyzing the floc size distribution. Considering the size distribution of particles as the criterion for selecting optimum polymer dosage, a dose of 0.5 mg/l appears to be the optimum for both of these polymers for the coagulation of 75 mg/l bentonite suspension. For the same suspensions, the optimum dosages determined from jar tests and electrophoretic mobility measurements, as reported in Table 6, were 0.05 and 0.2 mg/l

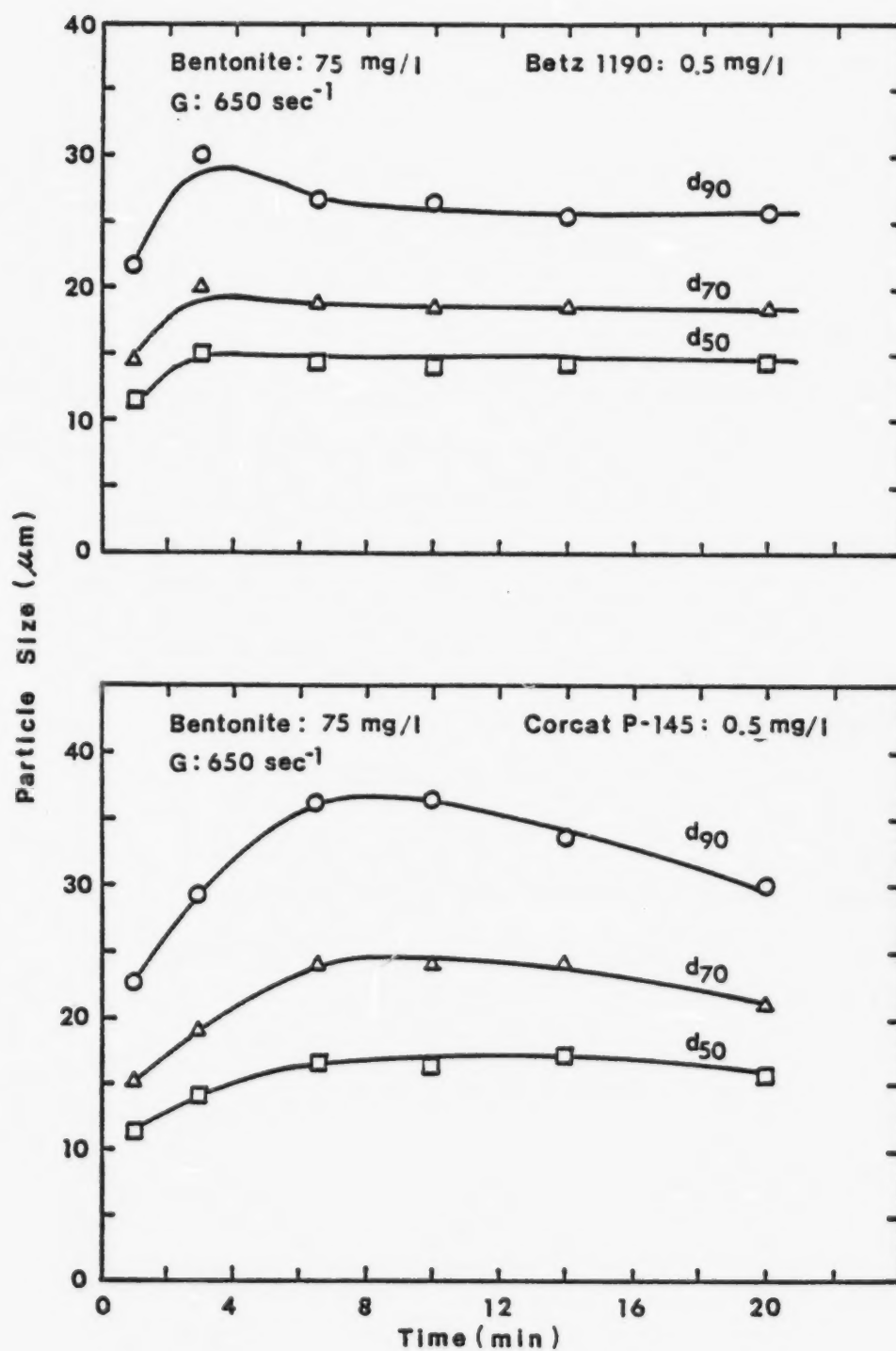


Fig. 17. Effect of Duration of Rapid Mix on Floc Size for 75 mg/l Bentonite and at $G=650 \text{ sec}^{-1}$

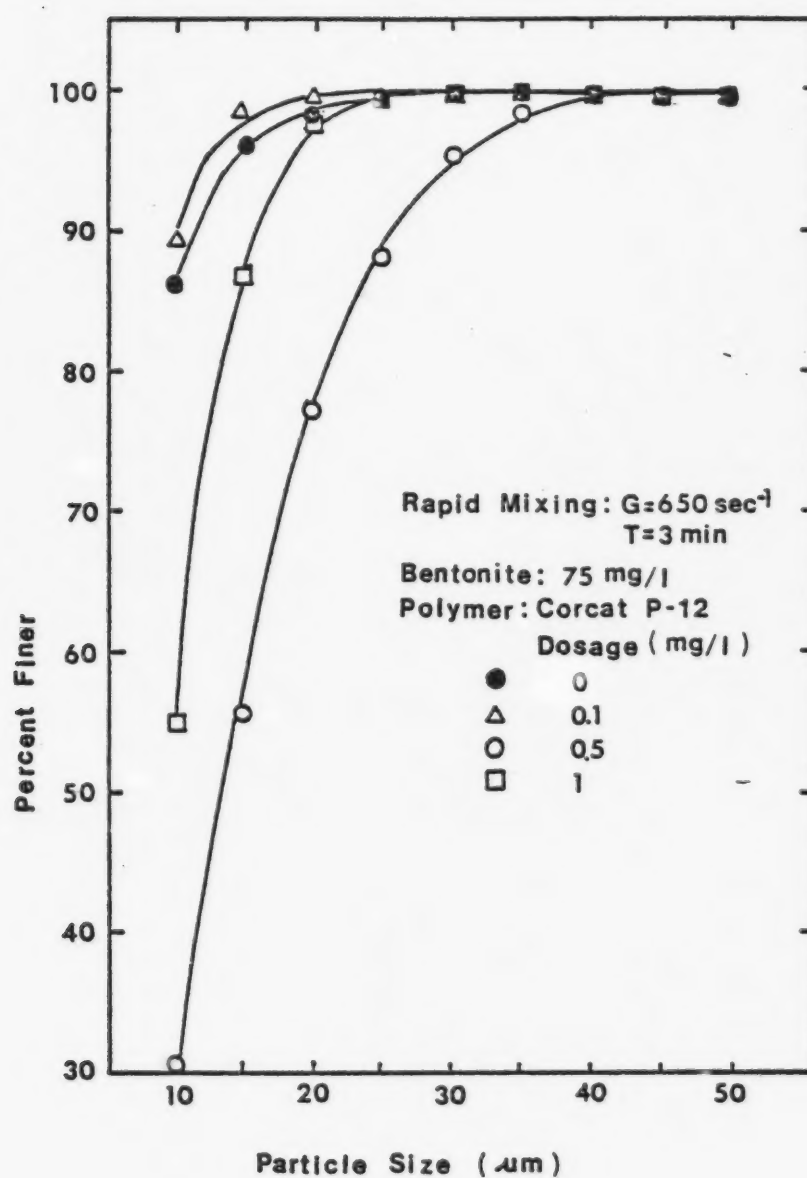


Fig. 18. Particle Size Distribution at Different Dosages of Corcat P-12 (Rapidly mixed for 3 minutes at $G=650 \text{ sec}^{-1}$. No slow mixing)

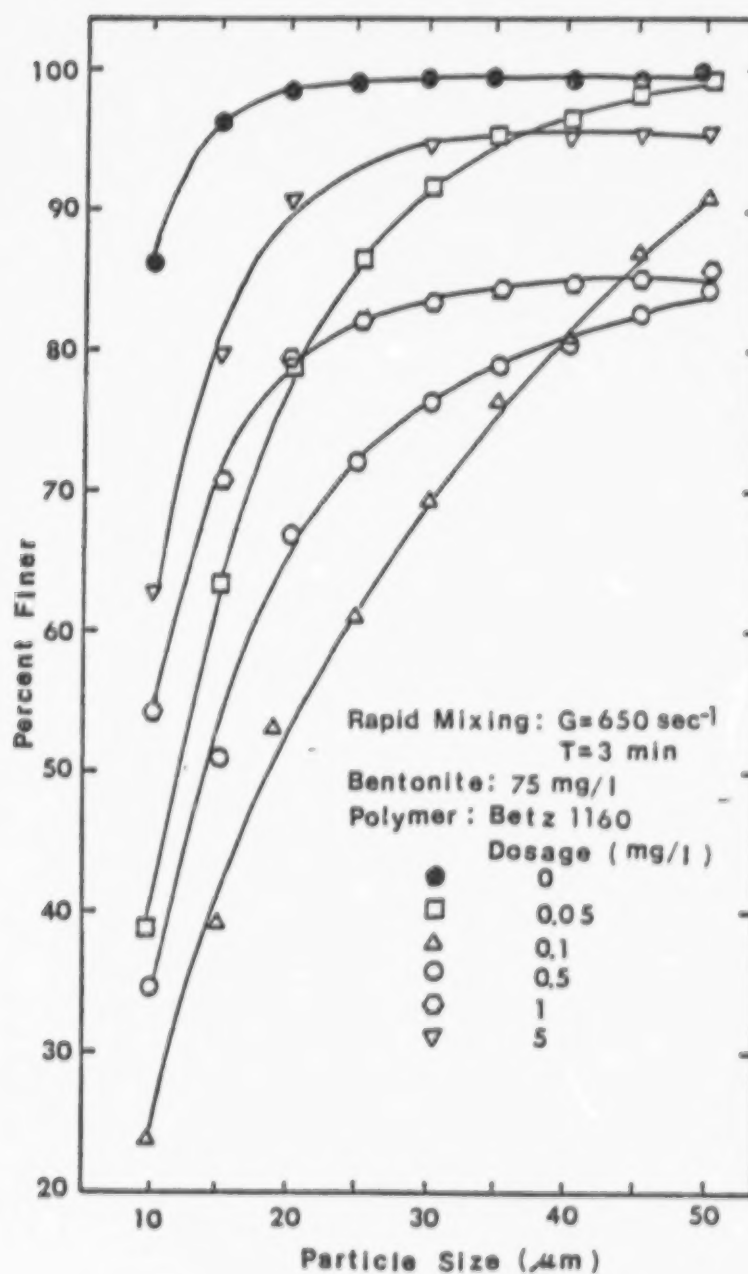


Fig. 19. Particle Size Distribution at Different Dosages of Betz 1160 (Rapidly mixed for 3 minutes at $G=650 \text{ sec}^{-1}$. No slow mixing)

for Corcat P-145 and Betz 1160, respectively. The observed lower values for dosages using jar tests was because of the slow agitation and settling that were allowed to occur in jar tests but not in studies involving particle count alone. For jar tests, a rapid mixing for 1 min. at $G=270 \text{ sec}^{-1}$ was followed by slow mixing at $G=40 \text{ sec}^{-1}$ for 20 min., and finally, settling for 30 min. Dosage based on particle counts may be best suited for direct filtration where premixing of polymers for short durations followed by no slow mixing closely parallel the experiments described in Figures 18 and 19.

The behavior of polymer-particle interaction under different initial mixing conditions, as measured by particle size distribution at various dosages, is shown in Figure 20. The particle sizes corresponding to 90, 70 and 50 percent finer on count basis are plotted as a function of dosage for various initial G's. Figure 20 clearly demonstrates that the optimum polymer dosage, about 0.4 mg/l for Corcat P-145, is independent of initial mixing energy. Again, the criterion of optimum dosage used in this analysis was particle size. Similar conclusions were drawn for all other cationic polymers investigated.

The effect of rapid mixing intensity on particle size distribution has been shown in Figure 21 for three polymers with molecular weight varying from 1200 to 3×10^6 . Optimum dosages, as determined from experiments described in Figure 20, were used. For low molecular weight polymers, Corcat P-12 and Corcat P-145, the G for rapid mixing had an insignificant effect on size distribution of particles. Apparently, up to a molecular weight of 40,000, a G value of 300 to 400 sec^{-1} is sufficient to obtain optimum size distribution. For high molecular weight polymers, such as Betz 1160, G plays a significant role. A G of 650 sec^{-1} appears to give optimum coagulation. At velocity gradients higher than 650 sec^{-1} , breakup of flocs result. It is conceivable that at higher colloid concentrations,

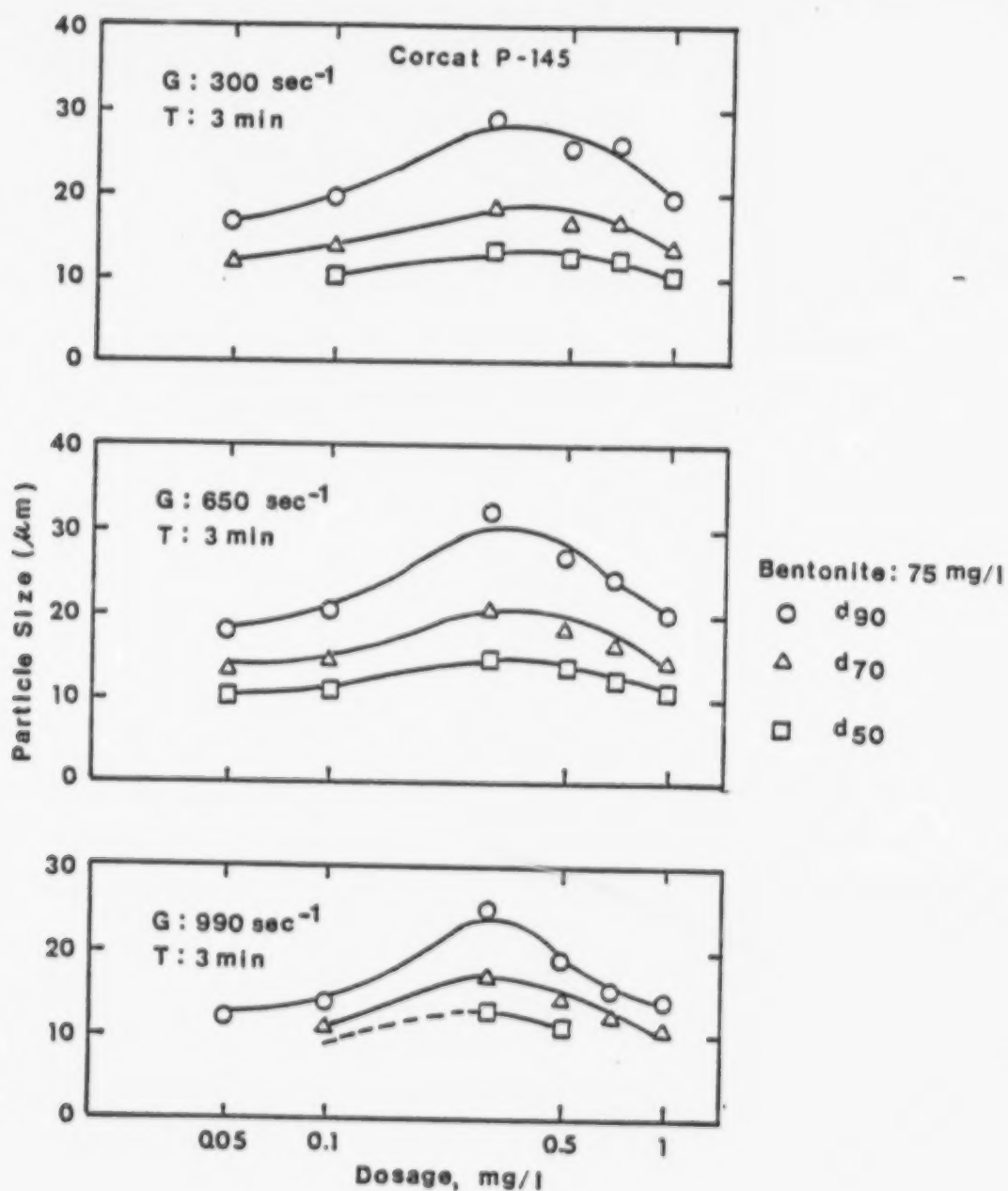


Fig. 20. Particle Size Distribution as a Function of Polymer Dosage and Rapid Mixing Intensity (Corcat P-145. Rapid mixing for 3 min. No slow mixing)

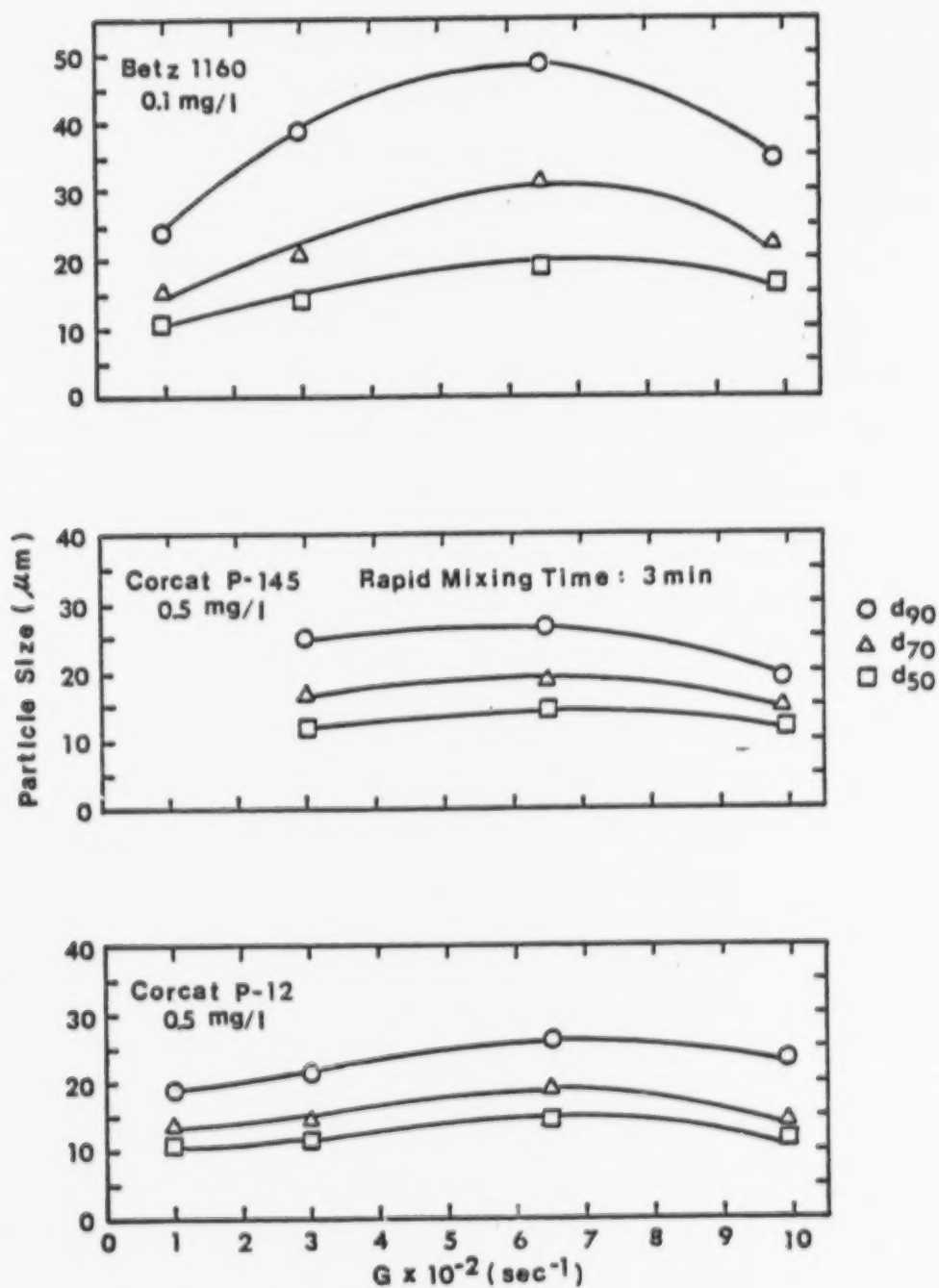


Fig. 21. Effect of Rapid Mixing Intensity on Particle Size at Optimum Dosage (Mixing duration = 3 min. No slow mixing)

optimum rapid mixing intensity may be somewhat lower. It should also be noted that the size of flocs obtained with high molecular weight polymers are generally larger. This is specifically the reason why very high molecular weight polymers should not be used in direct filtration. The filter runs will be shortened because of excessive headloss and not for solids breakthrough. In this study, an initial rapid mixing for 3 minutes at a G of 650 sec^{-1} was used in all subsequent flocculation experiments.

Since all flocculation experiments were primarily geared toward developing criteria for rapid mixing intensity and duration for use in direct filtration, only limited experimentation was done on actual flocculation by slow agitation. Figure 22 presents results of these studies for three cationic polymers. The criterion used to measure efficiency of flocculation was particle size distribution. In all of these experiments, only optimum dosages of polymers, as determined during rapid mixing, were used. Initial mixing was done for 3 minutes at a G of 650 sec^{-1} followed by slow agitation at a G of 60 sec^{-1} . At various times during slow agitation, samples of well mixed floc suspension were analyzed for size distribution. It should be noted that a value of zero on the time axis marks the end of 3-minute rapid mix period and, concurrently, the beginning of slow mixing period. Reviewing the data, it becomes clear that flocculation is virtually complete at the end of the rapid mixing period for low molecular weight polymers, Corcat P-12 and P-145, while slow mixing definitely encourages further growth in floc size for high molecular polymer Betz 1160 ($MW = 3 \times 10^6$). The 90-percentile size increases to a maximum of 70 microns after 10 minutes of slow mixing at a G of 60 sec^{-1} ($Gt = 3.6 \times 10^4$). Continuing slow mixing beyond 10 minutes caused floc break up. After 10 minutes of slow mixing 50 percent of the particles had a size larger than 21 microns. Although this may be a desirable goal in flocculation, such large size flocs will invariably lead to high head loss in deep filters. It

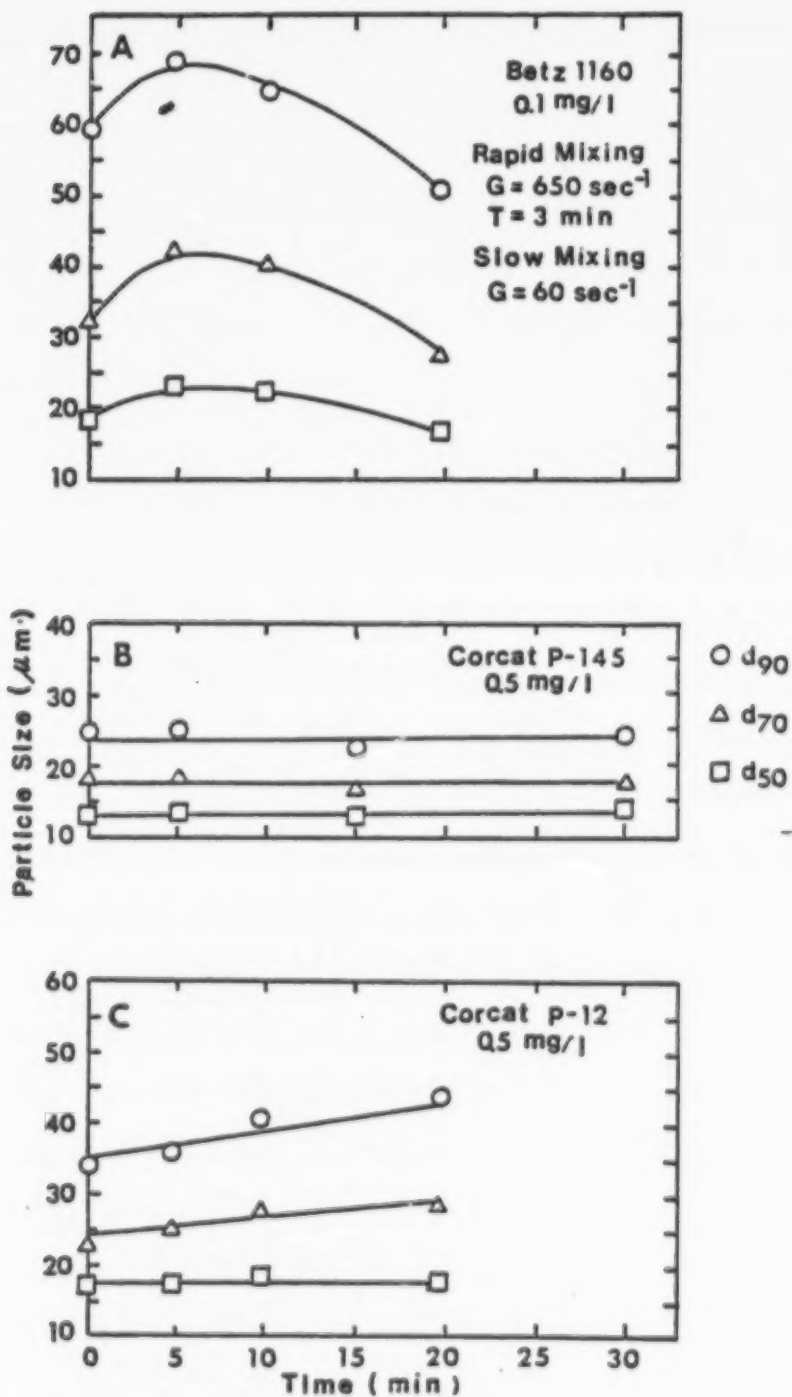


Fig. 22. Effect of Slow Mixing on Particle Size (Rapid mixing at $G=650 \text{ sec}^{-1}$ for 3 min. and slow mixing at $G=60 \text{ sec}^{-1}$)

further confirms the utility of using low molecular weight cationic polymers that allow significant bed penetration by the resultant smaller size flocs and permit longer filter runs.

3. Floc Strength

Many investigators have attempted to develop criteria for measuring floc strength. It is common knowledge that for a direct filtration system to work optimally, strong flocs must be produced in the filter. As a dynamic filter clogs, it will cause failure of large, loosely bound flocs by shear that develop in the pore spaces. In this study, attempts were made to simulate a high shear condition, following the initial formation of flocs, to determine the effect of expected high shearing stress on flocs in a clogging filter bed. The results of experiments on floc strength are shown in Figure 23. In all samples, except the blank where no polymer was added, an optimum dosage of 0.1 mg/l of Betz 1160 was added and rapid mixed at $G=650 \text{ sec}^{-1}$ for 3 minutes. All samples were slowly mixed for an additional period of 20 minutes at $G=60 \text{ sec}^{-1}$. One of the four samples was analyzed for particle size at the end of the slow-mix period. The remaining three samples were subjected to a secondary rapid mixing at G's of 650, 900 and 1300 sec^{-1} for an additional 3 minutes and then these suspensions were analyzed for particle sizes. The sample subjected to a secondary rapid mixing at a G of 650 sec^{-1} , yielded a particle size distribution which was essentially unaltered. The sample subjected to a secondary rapid mixing at G's of 900 and 1300 sec^{-1} showed definite evidence of floc breakage. A velocity gradient of 1300 sec^{-1} corresponds to a shearing stress of 11.7 dyne/sq cm or is equivalent to an energy of 6.24×10^{-9} Kcal/mole of water which is much smaller than the energy of weak van der Waals forces or hydrogen bonding (about 5 Kcal/mole). Seemingly, high shear will cause floc break up although shear energy may be much smaller than that for H-bonding. Possibly, the flocs are held together by surface tension and, based on such

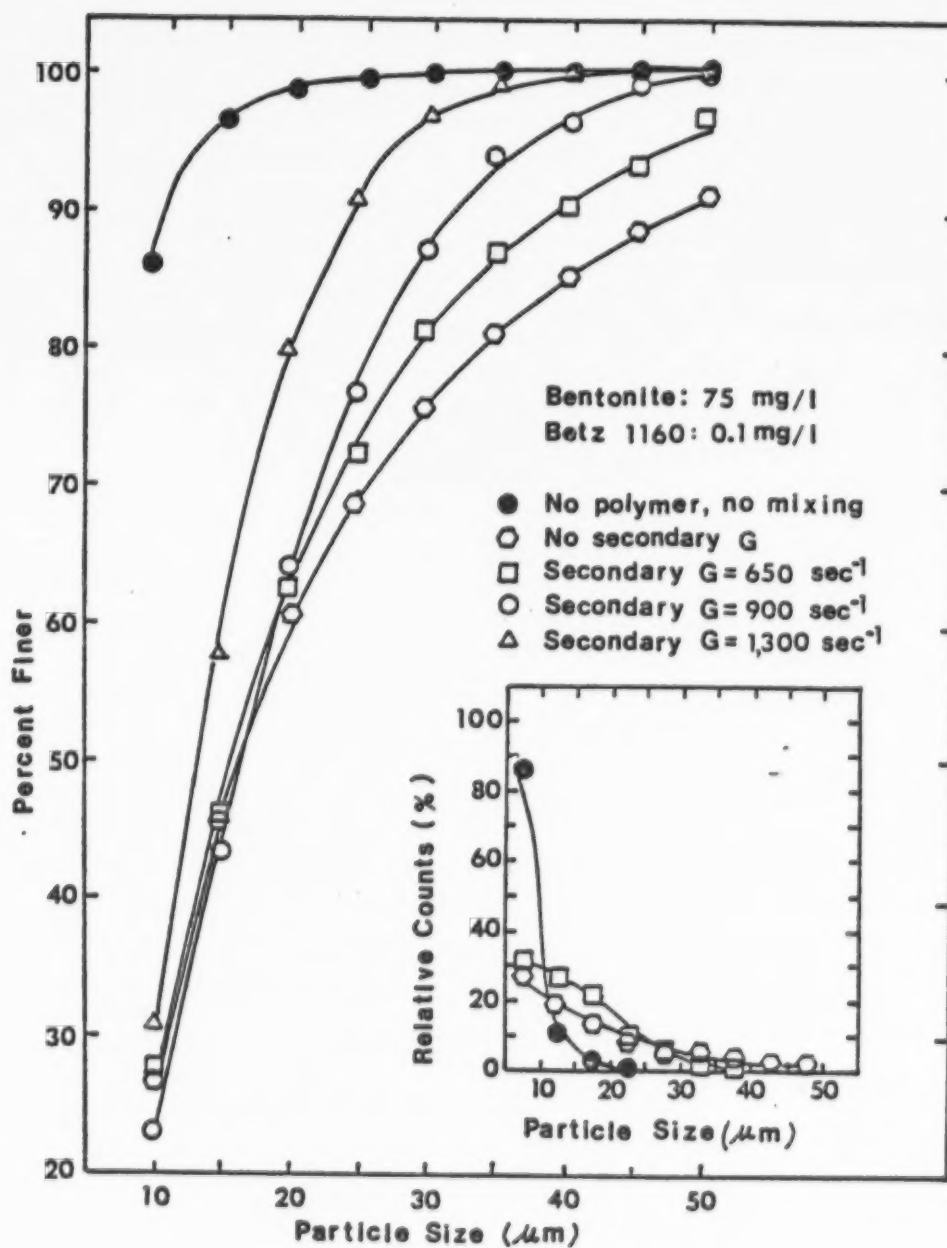


Fig. 23. Effect of Post-Flocculation High G on Floc Breakup
(Rapid mixing for 3 min. at $G = 650 \text{ sec}^{-1}$, slow mixing
at $G = 60 \text{ sec}^{-1}$ for 20 min.)

a hypothesis, breakage will occur if 72 dyne/cm of surface tension (between air and water) is overcome.

In a clogging filter, the velocity gradient and hence the shear stress change gradually as the headloss builds up. This was simulated in batch flocculation tests using a high molecular weight (Betz 1160) and a low molecular weight polymer (Corcat P-145). Both experiments were conducted using a 75 mg/l bentonite suspension and optimum polymer dosages. The results are shown in Figures 24 and 25 for Betz 1160 and Corcat P-145, respectively. The bentonite suspension was mixed with polymer for 3 minutes at a G of 650 sec^{-1} and then G was decreased to 220 sec^{-1} for the next 20 minutes, and so on up to a final G of 650 sec^{-1} . This is shown in Figures 24B and 25B. At the midpoint of each 20-minute period, a sample of the well mixed suspension was analyzed for particle size distribution. These distributions are shown in Figures 24A and 25A. The symbols used for different cumulative distributions in part A correspond to those used in part B. In Figures 24C and 25C, the 90, 70 and 50 percentile sizes are plotted as a function of time which, in turn, corresponds to the midpoint of a given constant G period in Figures 24B and 25B. From the results in Figure 25, it appears that no break up of floc should result in a filter bed within the range of headloss normally encountered when low molecular weight polymers are used. The fact that high molecular weight polymers produce larger flocs, comparing Figures 24C and 25C at 3 minutes, i.e., after rapid mixing, leading to gradual deterioration of floc size, becomes the primary reason for the observed effluent quality degradation during clogging in direct filters. The percentage of particles in the effluent from such a filter will gradually increase as the filter run progresses and headloss builds up.

The major findings from the studies on velocity gradient and its effect of floc size can be summarized as below

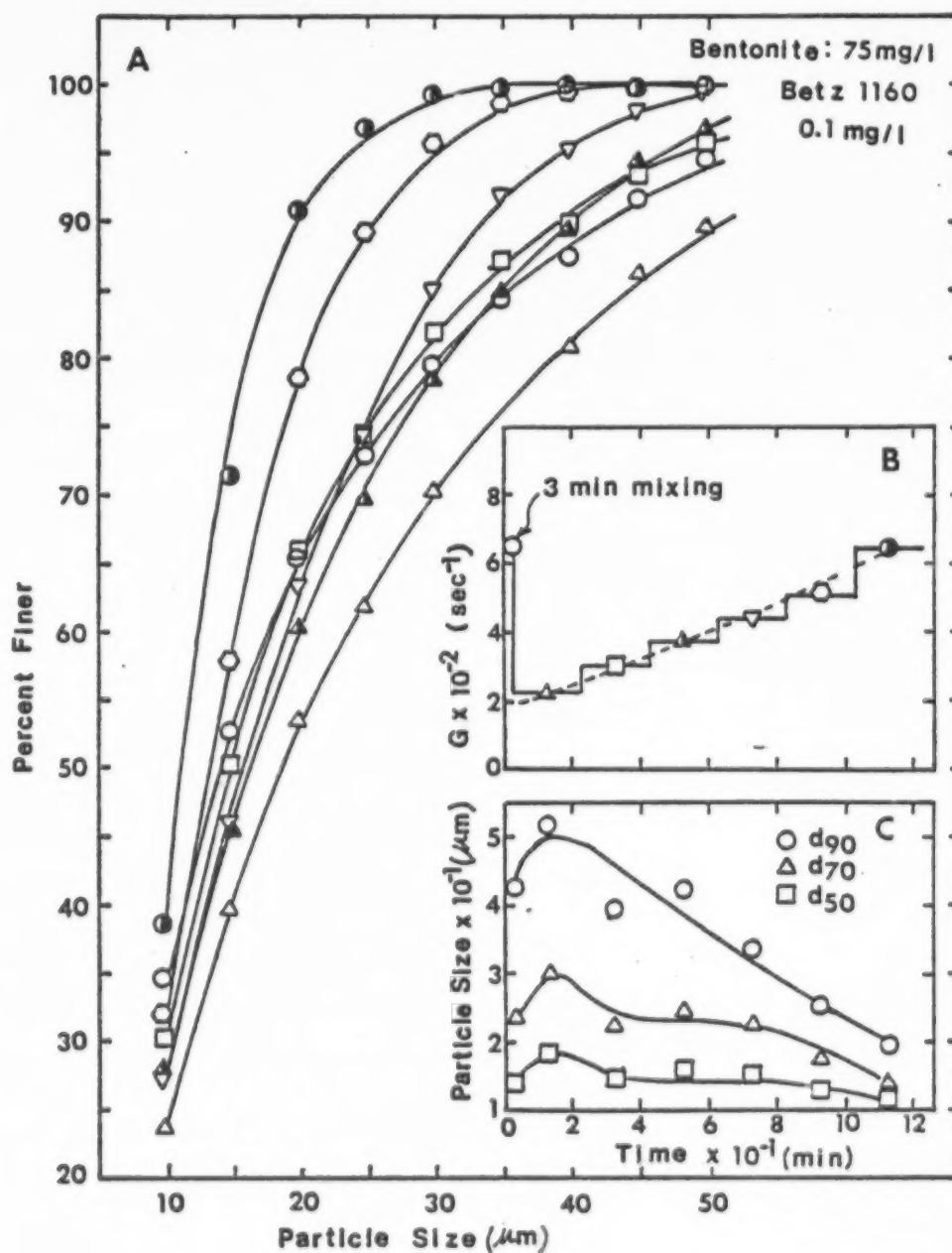


Fig. 24. Effect of Gradual Increase in G on Floc Size (Betz 1160)

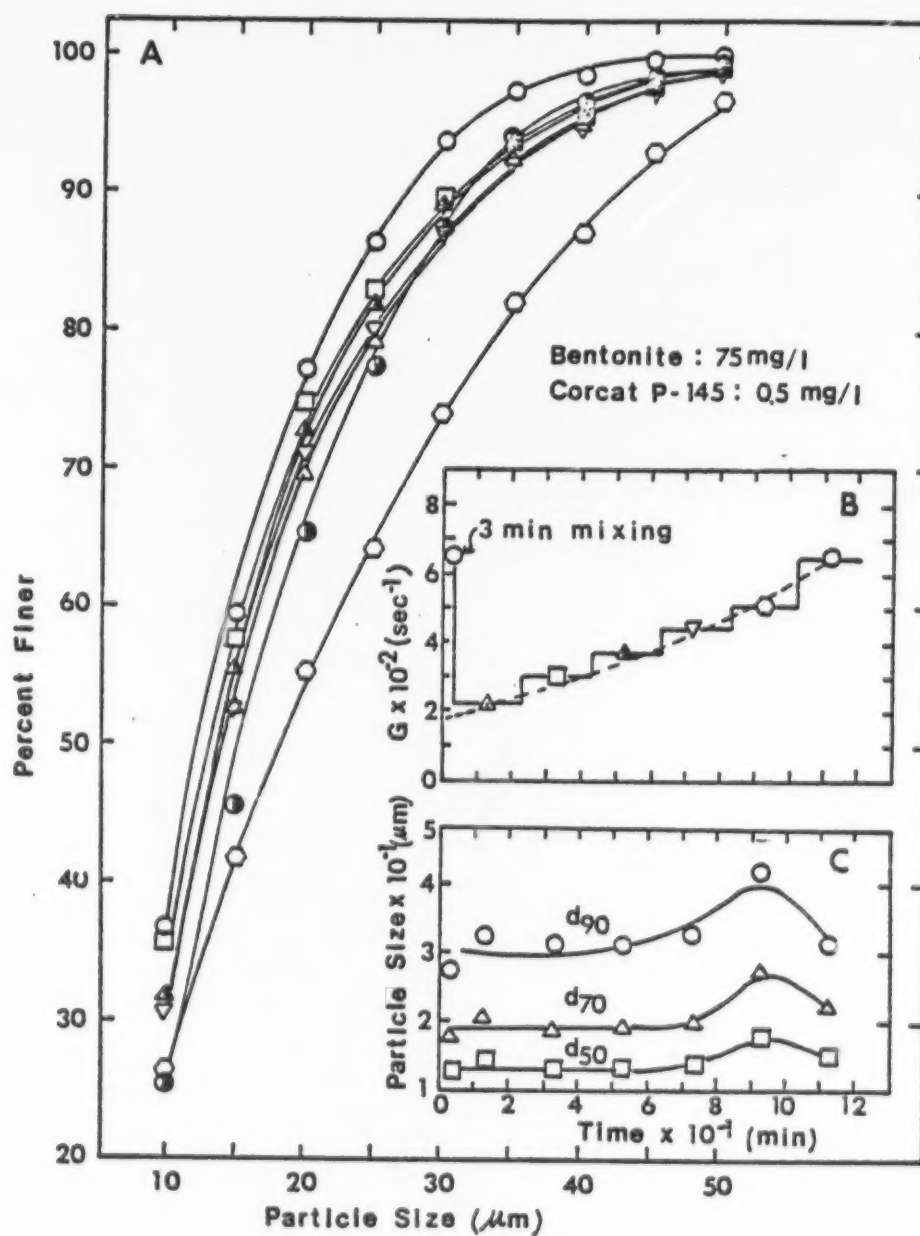


Fig. 25. Effect of Gradual Increase in G on Floc Size (Corcat P-145)

- a) The initial rapid mixing is essentially complete within 3-8 minutes and the velocity gradient of rapid mix may vary from a low value of 300 to a high of 650 sec^{-1} for polymer molecular weights varying from 1200 to 3×10^6 .
- b) Polymer dosage is independent of velocity gradient of mixing for low molecular weight polymers. A weak dependence was noted for high molecular weight polymers. However, the dosage for a given fractional removal of turbidity, would conceivably depend on the product Gt .
- c) For low molecular weight cationic polymers, flocculation is essentially complete after rapid mixing, no further slow mixing is required. Thus, these are ideally suited for direct filtration. Bed penetration should be excellent and headloss development small.
- d) Break up would result by subjecting preformed flocs to a secondary high shear. There is also some evidence that in clogging filters, gradual increase in the velocity gradient within the filter may lead to the break up of preformed floc when high molecular weight polymers are used.
- e) The selection of optimum polymer dosage for direct filtration based on particle size distribution appears to be a better method than jar test or measurement of electrokinetic potential, although the former tends to give higher values.

G. Optimum Dose from Refiltration Theory.

Refiltration method was employed to obtain optimum dosage of Cat-Floc for the flocculation of three different concentrations of bentonite, 0.5, 1.0 and 2.0 gm/l. In all cases, a given dosage of polymer was rapidly mixed with the bentonite suspension for 3 minutes at a $G=650 \text{ sec}^{-1}$ before filtration. One of the disadvantages of this method is that the results are unreliable for dilute suspensions because a suitable cake cannot be formed. Time to refilter 25 ml (10 ml to 35 ml) of filtrate was noted for suspensions having no polymer and those treated with various dosages of polymer. Plots were made in accordance with Eq. 13 where C_0 is the dosage of polymer in mg/l and Q and Q_0 are refiltration rates in ml/sec for samples with polymers and no polymer, respectively. Typical results for the refiltration of polymer-mixed bentonite suspension with a colloid concentration of 2 g/l are shown in Figure 26. The data for turbidity and that for the functional coverage of colloid surface (θ) are also shown on the same graph. The computation of the values for θ at different dosages of polymer will be discussed later. The turbidity measurements were made on supernatant samples following 20 minutes quiescent settling. Concurrently, a fraction of each sample was removed immediately after rapid mixing and analyzed for particle size distribution. Typical results are shown in Figure 27 for the 2 g/l bentonite suspension. Based on particle size distribution results, 50 mg/l appears to be the optimum dosage of Cat-Floc. The values of percent surface coverage θ were obtained by using Equations 2 to 4. The values of r_m and K in these equations were obtained from a Langmuir plot of data for equilibrium concentration of polymer and the amount of polymer used during the refiltration experiments reported in Figure 26. The form of the Langmuir isotherm used are shown in Equations 1 and 6. In all calculations gravimetric concentration of colloid was used instead of its surface con-

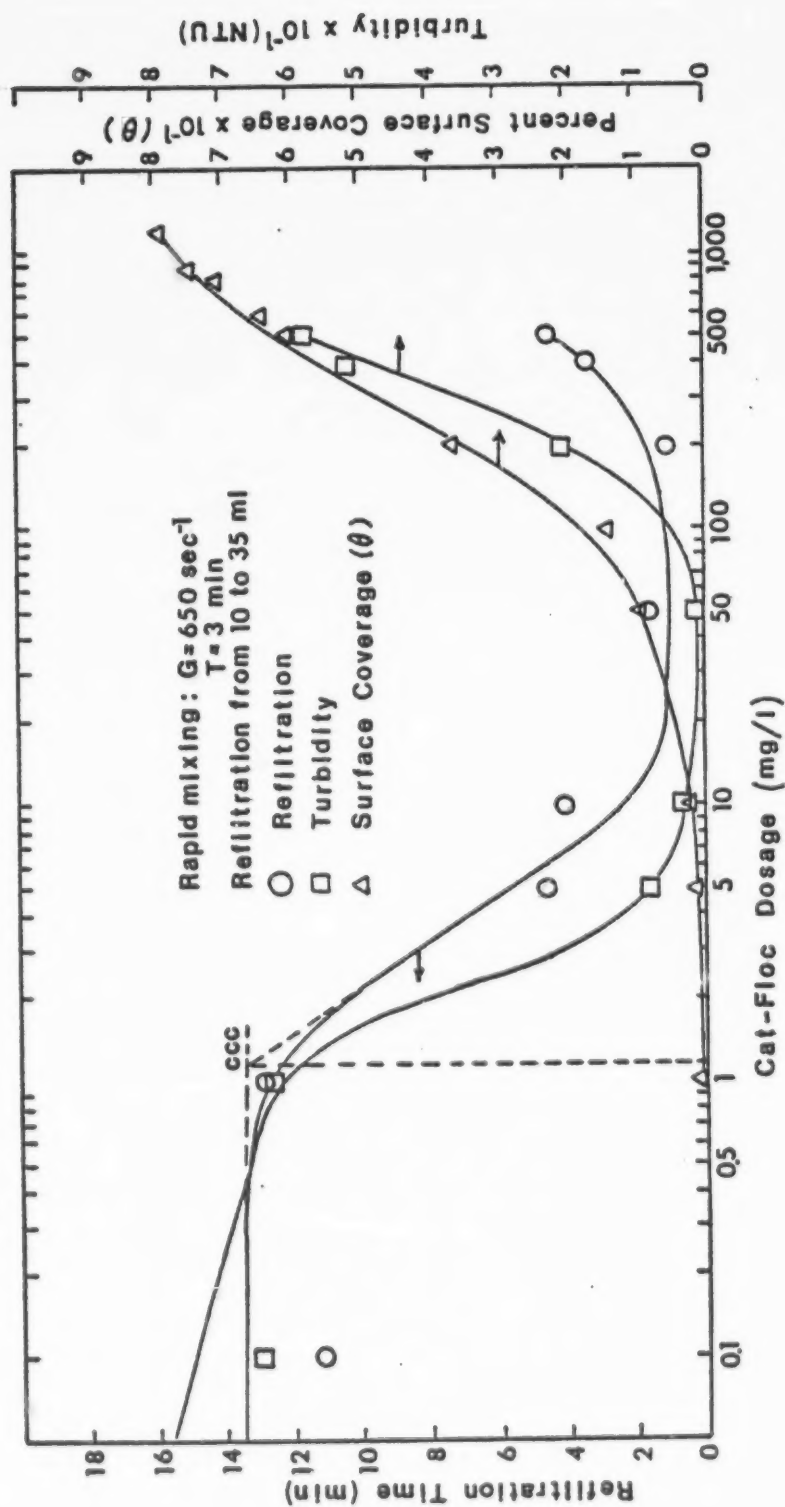


Fig. 26. Refiltration of 2 g/l Bentonite Suspension Flocculated with Cat-Floc

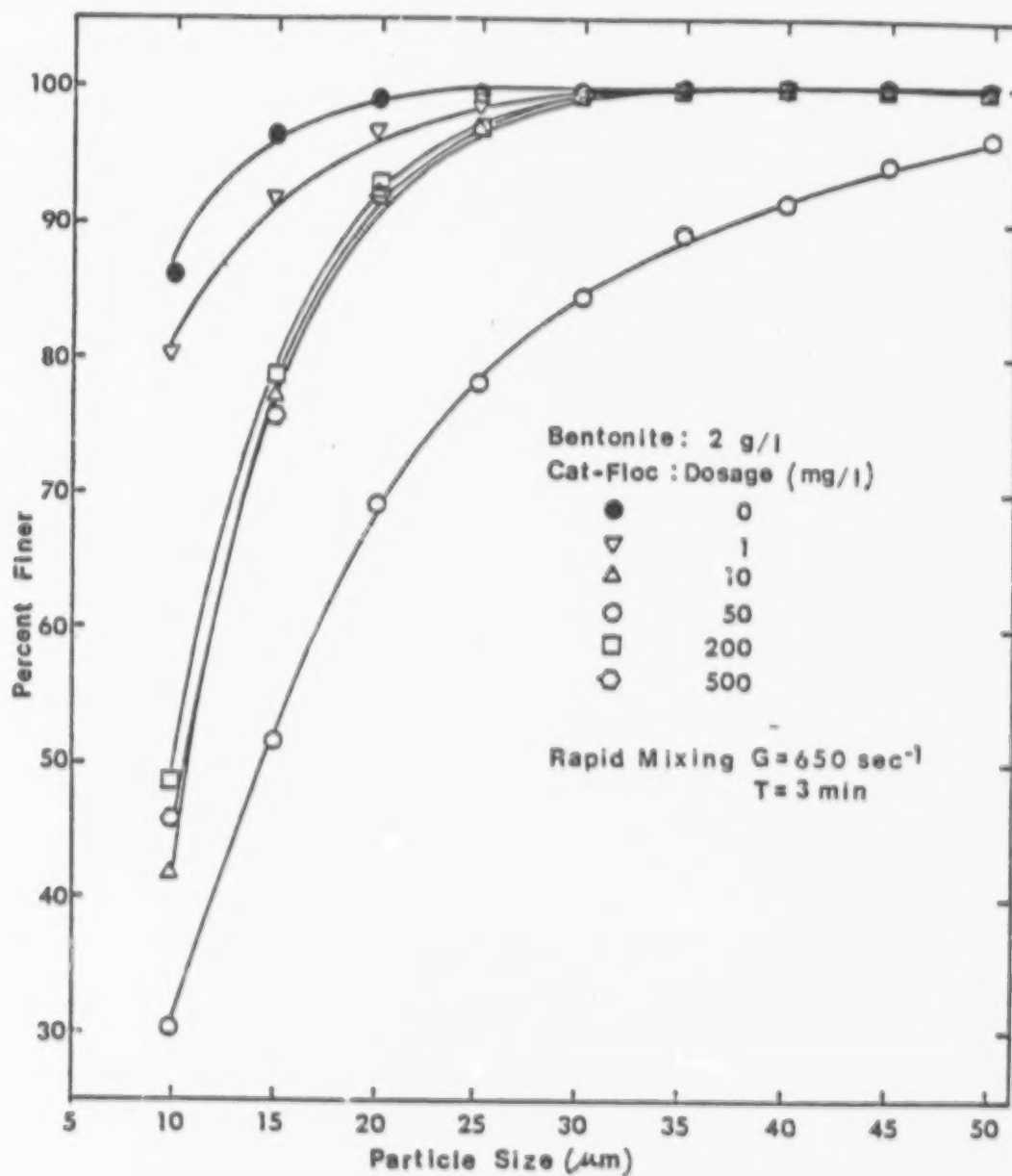


Fig. 27. Particle Size Distribution for Bentonite at Various Cat-Floc Dosages (Rapid mixing for 3 min. at $G = 650 \text{ sec}^{-1}$.)

centration, S. The excess polymer remaining at equilibrium following rapid mixing of bentonite-polymer mixture were determined from titration with a standard solution of negatively charged PVSK. First the flocculant colloid-polymer matrix was centrifuged at 1200 g for 20 minutes and the centrifugate sample was analyzed for equilibrium polymer concentration (C_e). The amount of polymer adsorbed (C_a) was obtained by subtracting C_e from the concentration added. An alternate method developed by Dow Chemical Company (39) was also used for determining equilibrium concentration of polymer for adsorption experiments with Corcat Polymers (poly-ethylenimine). The method involves the complexation of residual poly-ethylenimine with 1, 2 naphthoquinone-4-sulfonic acid and measuring the colored complex at a wave length of 450 nm. Beer-Lambert Law is obeyed in the concentration range of 0 to 12 mg/l based on a 50 ml sample. The prescribed procedure calls for the use of a 0.05% 1,2 naphthoquinone-4-sulfonic acid and a 2% trisodium phosphate solution. However, considerable difficulty arose in measuring color with 0.05% solution of the complexing agent. The method was modified to use 0.5% solution of the coloring complex instead. This modification gave satisfactory results.

Langmuir plots were obtained for the adsorption of Cat-Floc on 2 g/l bentonite suspension using both Equations 1 and 6 are presented in Figure 28A and 28B respectively. The values of maximum adsorption capacity (saturation capacity, Γ_m) and Langmuir's equilibrium constant, K, obtained from both plots were very similar. These isotherm constants were then used to obtain the values of fractional coverage of colloids as shown in Table 7 and also in Figure 26. Similar refiltration studies were done on 2 g/l bentonite suspension using Corcat P-12 (MW = 1200). From linearized Langmuir plots the saturation adsorption, Γ_m and equilibrium constant, K, were estimated as 0.143 mg/mg and 0.12, respectively. Using these constants

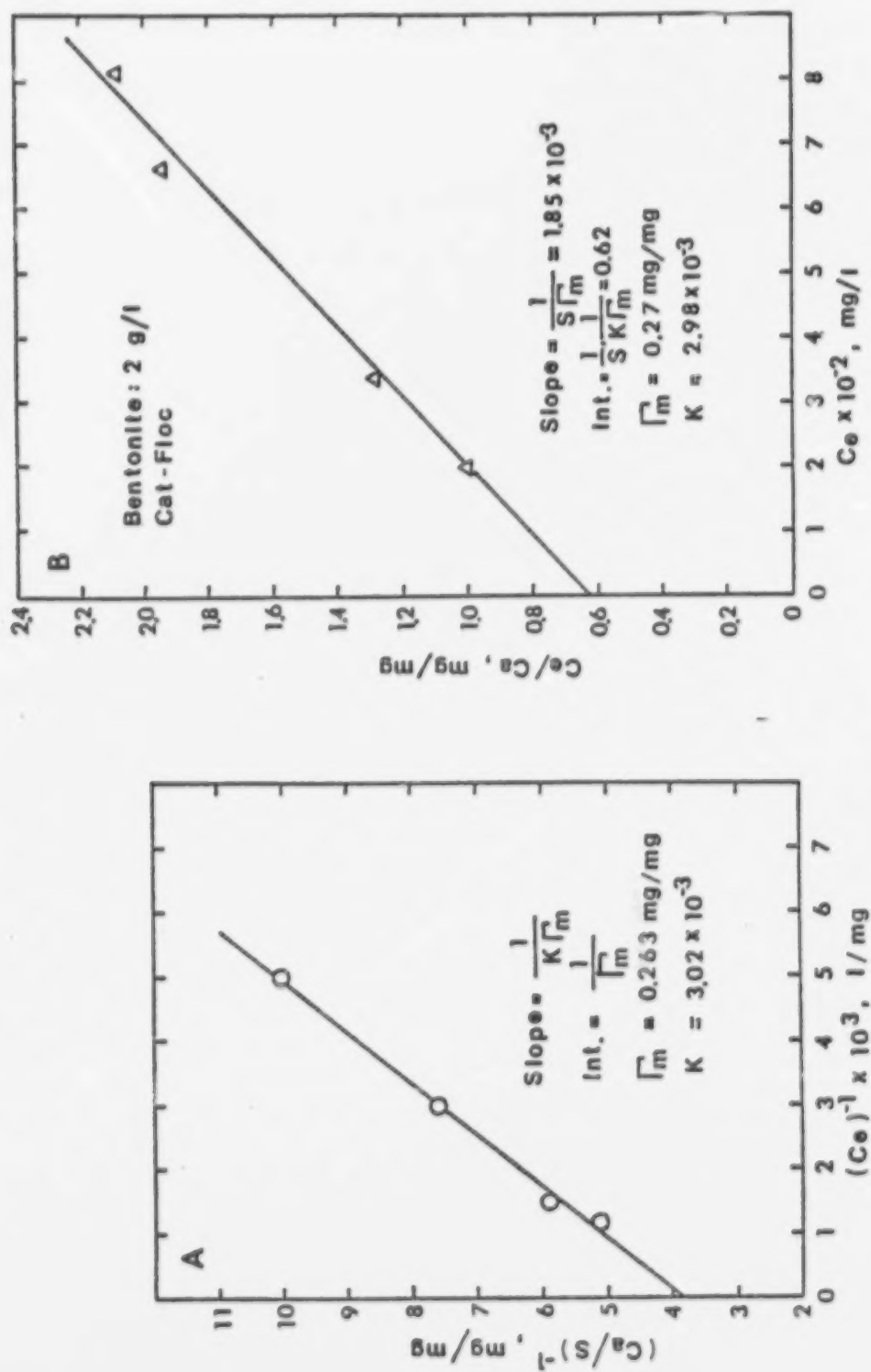


Fig. 28. Linearized Langmuir Plots for the Sorption of Cat-Floc on Bentonite (2 g/l)

Table 7. Calculations for Langmuir Isotherm and θ for Bentonite Suspension ($S=200$ mg/l; 1600 m²/l)

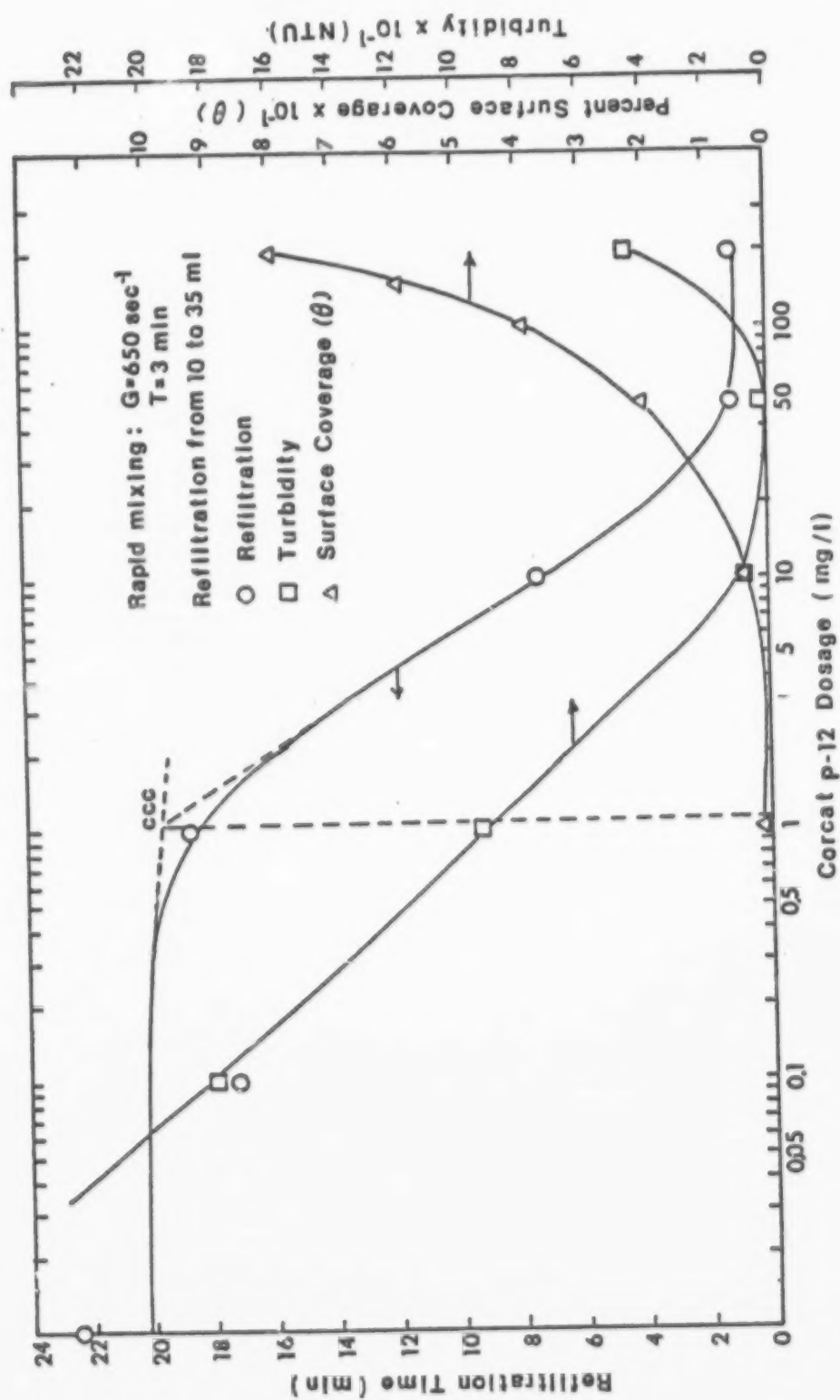
Polymer Added ($C_{t\theta}$) (mg/l)	Eq/m. Conc. of Polymer (C_e) (mg/l)	Polymer Adsorbed (C_a) (mg/l)	$\frac{C_e}{C_a}$ (mg/l)	C_e^{-1} (l/mg)	$\left(\frac{C_a}{S}\right)^{-1}$ (mg/mg)	θ^*	Remarks for θ
0.01	nil	0.01	-	-	2×10^5	1.85×10^{-5}	Eq. 3
0.1	nil	0.1	-	-	2×10^4	1.85×10^{-4}	Eq. 3
1.0	nil	1.0	-	-	2×10^3	1.85×10^{-3}	Eq. 3
5.	nil	5.	-	-	400	9.3×10^{-3}	Eq. 3
10.	nil	10.	-	-	200	1.85×10^{-2}	Eq. 3
50.	5	45	.11	200×10^{-3}	44.4	9.3×10^{-2}	Eq. 3
100	10	90	0.11	100×10^{-3}	22.2	0.14	Eq. 3
200	20	180	0.11	50×10^{-3}	11.1	0.37	Eq. 3
400	200	200	1.0	5×10^{-3}	10.	0.28	Eq. 2
500	302	198	1.52	3.3×10^{-3}	10.1	0.60	Eq. 4
600	338	262	1.29	3×10^{-3}	7.6	0.64	Eq. 4
800	605	195	3.10	1.6×10^{-3}	10.2	0.71	Eq. 4
1000	660	340	1.94	1.5×10^{-3}	5.9	0.75	Eq. 4
1200	810	390	2.08	1.2×10^{-3}	5.1	0.78	Eq. 4

* Calculated using isotherm constants obtained in Figure 288.

the fractional surface coverage of θ were calculated. Figure 29 shows results of refiltration studies with Corcat P-12. Refiltration results for the same bentonite suspension using another polymer, Corcat P145 ($MW = 4 \times 10^4$) are presented in Figure 30. The Langmuir adsorption plot yielded a value of 0.13 mg/mg for r_m and 5.23×10^{-2} for K . The amount of polymer adsorbed, C_a , was higher than the equilibrium concentration for all dosages of polymer and, accordingly, all values for θ were calculated using Eq. 3.

For all refiltration studies reported in Figures 26 to 30, the pH was kept constant at 8. These figures indicate that coagulation of bentonite does not occur at very low polymer concentrations, so that residual turbidity and refiltration time remain constant. Increasing polymer concentration above ccc induces significant coagulation, i.e., an increase in particle size, as seen in Figure 27, and decrease in refiltration time. High concentration of polymer restabilize the suspension with concomitant increase in turbidity, decrease in particle size (Figure 27), and increase in refiltration time. The maximum coverage for Corcat P-12, Corcat P-145, and Cat-Floc were calculated as 1.5×10^{-7} , 4.1×10^{-9} and 3.4×10^{-9} moles/ m^2 of colloid surface area, respectively. Reviewing the adsorption behavior of the three polymers, it can be said that at low dosages, up to about 50 mg/l, all three polymers followed linear stoichiometry with colloid surface concentration. For low molecular weight polymers, such as Corcat P-12 and P-145, this stoichiometry, as depicted by Eq. 3, was obeyed up to a dosage of 4.2×10^{-4} mole/l for a colloid surface concentration of 2 gm/l or $1600 m^2/l$. Coagulation and restabilization phenomena appeared to be independent of colloid surface concentration for high molecular weight polymers, such as Cat-Floc ($MW = 1 \times 10^5$), for dosages above 4×10^{-6} mole/l, as given by Eq. 4.

Typical calculations for obtaining optimum dosage from refiltration data, in accordance with Eq. 13, are presented in Table 8, for Cat-Floc



Fi. 29. Refiltration of 2 g/l Bentonite Suspension Flocculated with Corcat P-12

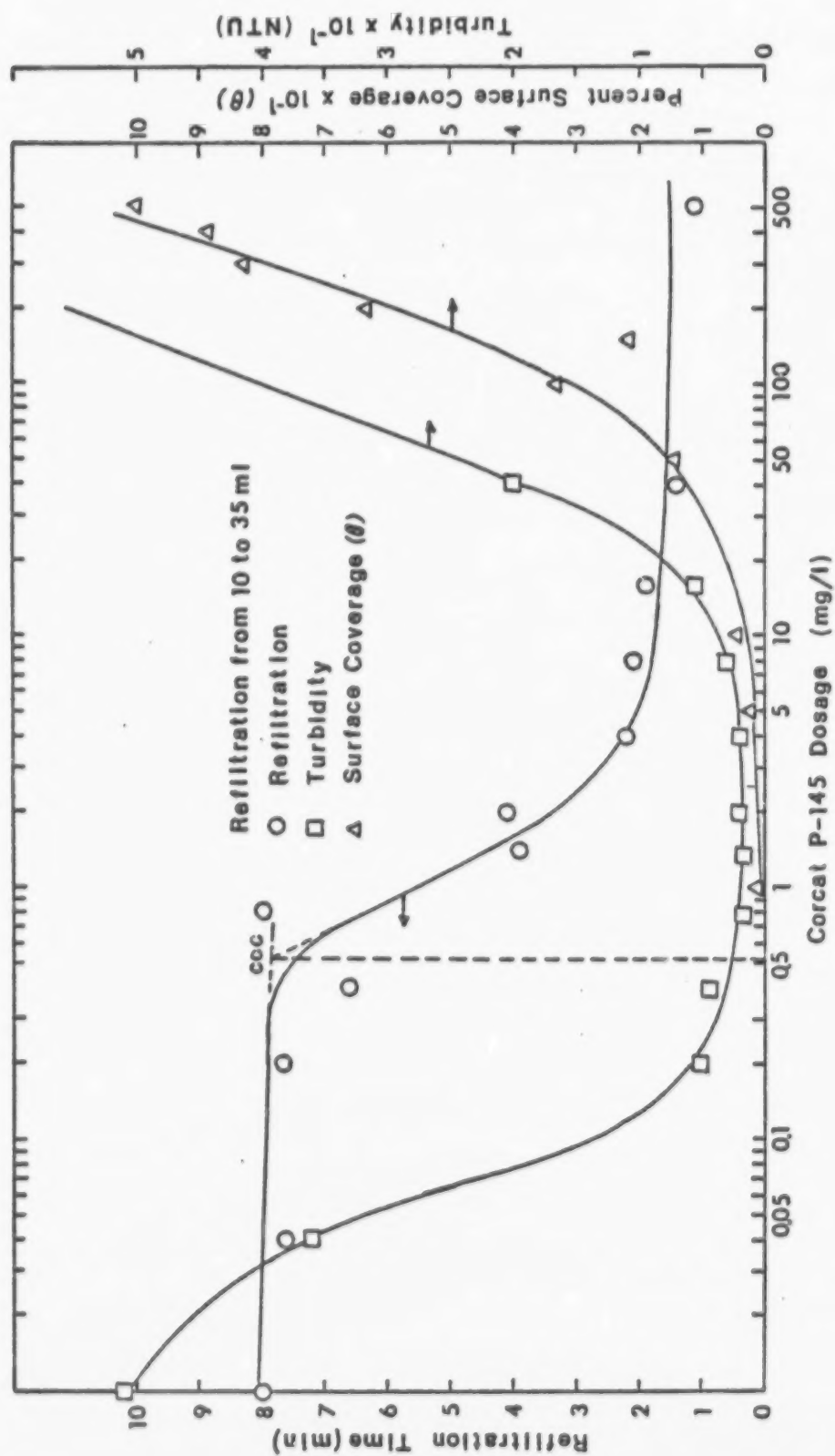


Fig. 30. Refiltration of 2 g/l Bentonite Suspension with Corcat P-145

Table 8. Calculations for Optimum Dosage from Refiltration Theory for Cat-Floc (Bentonite Concentration 1 g/l, $Q_0 = 3.1 \times 10^{-2}$ mg/l sec.)

C_0 mg/l	$C_0^{1/2}$	$t(\text{sec})^*$	$Q(\text{ml}/\text{sec})$	$(Q-Q_0)$	$(Q-Q_0)^{1/8}$	$\frac{C_0^{1/2}}{(Q-Q_0)^{1/8}}$
0.01	0.1	980	2.55×10^{-2}	-	-	-
0.1	0.32	901	2.77×10^{-2}	-	-	-
1	1	773	3.23×10^{-2}	0.13×10^{-2}	0.44	2.27
5	2.24	148	0.169	13.8×10^{-2}	0.78	2.87
10	3.16	142	0.176	14.5×10^{-2}	0.38	8.32
50	7.07	44	0.568	53.7×10^{-2}	0.92	7.68
100	10	98	0.255	22.4×10^{-2}	0.83	12.05
300	17.3	212	0.118	8.7×10^{-2}	0.74	23.38

*Time to filter from 10 ml to 35 ml

used on 1 g/l bentonite suspension. Similar data were obtained for 0.5 and 2 g/l bentonite suspensions using Cat-Floc. The linearized form of Eq. 13 was used to plot the straight lines for different colloid concentration as shown in Figure 31. Table 9 summarizes the results from this graphical procedure. The insert in Figure 31 shows the relationship between optimum dosage and bentonite concentration. Table 10 presents the characteristics of the three polymers used in the refiltration studies. From the values of θ , the fraction of surface sites covered, no specific conclusion can be drawn as to the steric interference of high molecular weight polymers or the flexibility of short chain molecules in occupying adsorption sites. The low degree of surface site coverage for low molecular weight polymers indicates relatively complete coverage of all adsorbing segments of the polymer chain. There is little evidence that saturation adsorption increases with molecular weight.

H. Charge Density and the Polymer Selection Process

The number of cationic charges per molecule of a polymer can be computed from the known charge density in coulombs/gm of polymer, its weight-average molecular weight, and the Avogadro's number. The weight-average molecular weight and the radius of gyration of polymers can be computed from light scattering data obtained from various sources in the literature. The optimum dosages of these polymers are correlated with molecular cationic charges in accordance with Eq. 5 as reported by Lindquist and Stratton (14). Instead of ccc , the values for optimum dosages as obtained from electrophoretic mobility were used in the plot (Fig. 32). The relationship assumes the following exponential form for the data points used,

$$\log (C_{opt}) = -1.2 - 0.92 \log z \quad (23)$$

$$\text{or } C_{opt} = \frac{0.063}{z^{0.92}} \quad (24)$$

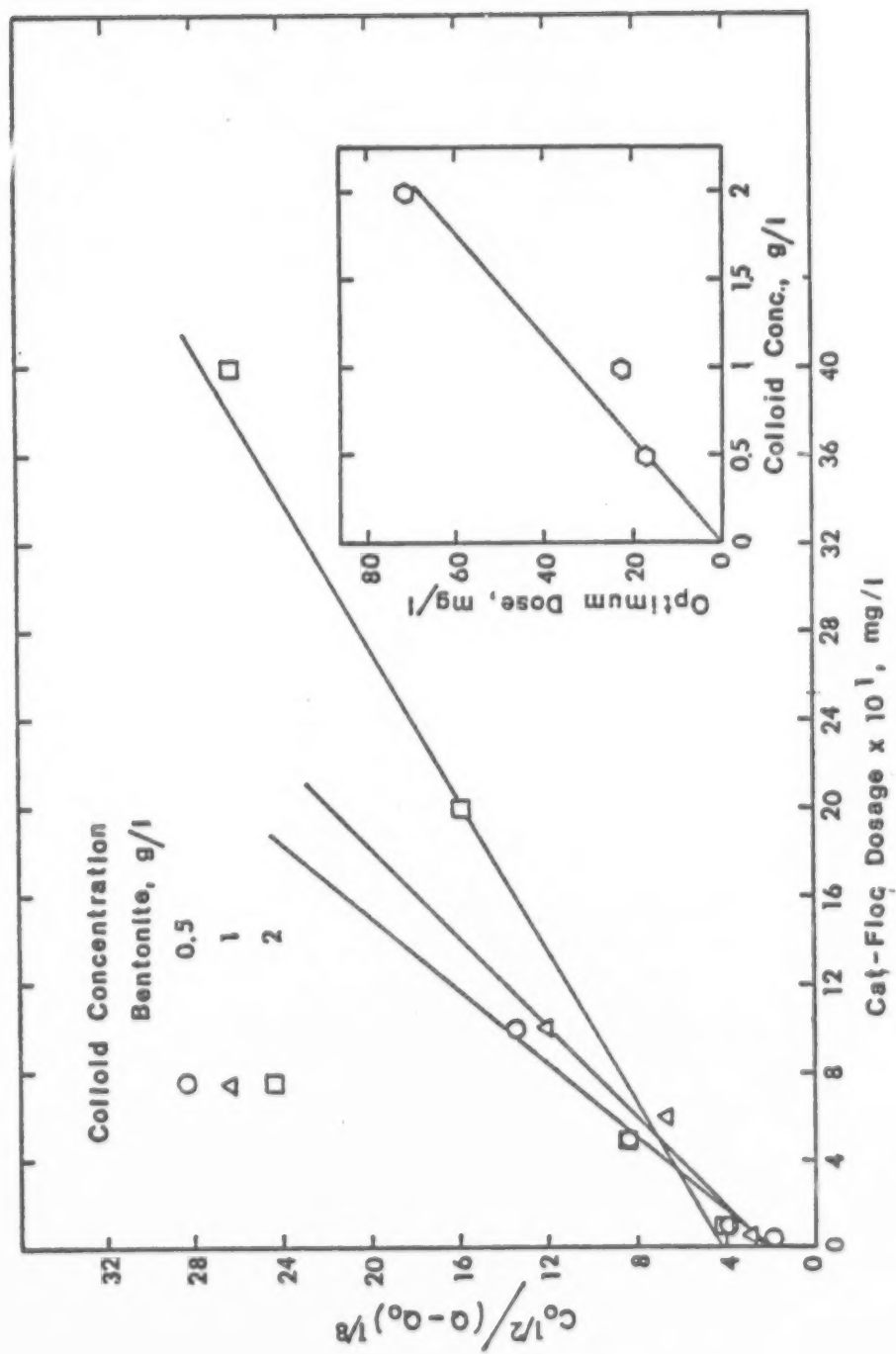


Fig. 31. Optimum Dosage of Polymer from Refiltration

Table 9. Summary of Graphical Procedure for Obtaining Optimum Dosage from Refiltration Theory for Cat-Floc.

Colloid Conc. (mg/l)	C_0 ml/sec	Intercept - (a)	Slope (p)	Opt. dose (a/p), (mg/l)
500	3.8×10^{-2}	2	0.12	16.7
1000	3.1×10^{-2}	2.2	0.1	22
2000	1.4×10^{-2}	4.2	0.059	71.2

Table 10. Characteristics of Polymers in Refiltration of Bentonite

Polymer	$\langle M \rangle_n$	CCC (mg/l)	C_{opt} (mg/l)	$\frac{\Gamma_m}{\text{mg/mg}}$	$\frac{\Gamma_m}{\text{moles/m}^2}$	K	θ_{opt}^* (%)
Corcat P-12	1200	1.1	18	0.143	1.5×10^{-7}	0.12	7
Corcap P-145	4×10^4	0.15	34	0.13	4.1×10^{-9}	0.052	12
Cat-Floc	1×10^5	1.15	66	0.27	3.4×10^{-9}	3×10^{-3}	10.6

* These values should be compared with $\theta_{opt} = 50\%$ as predicted by LaMer et. al. (6) in Eq. 12.

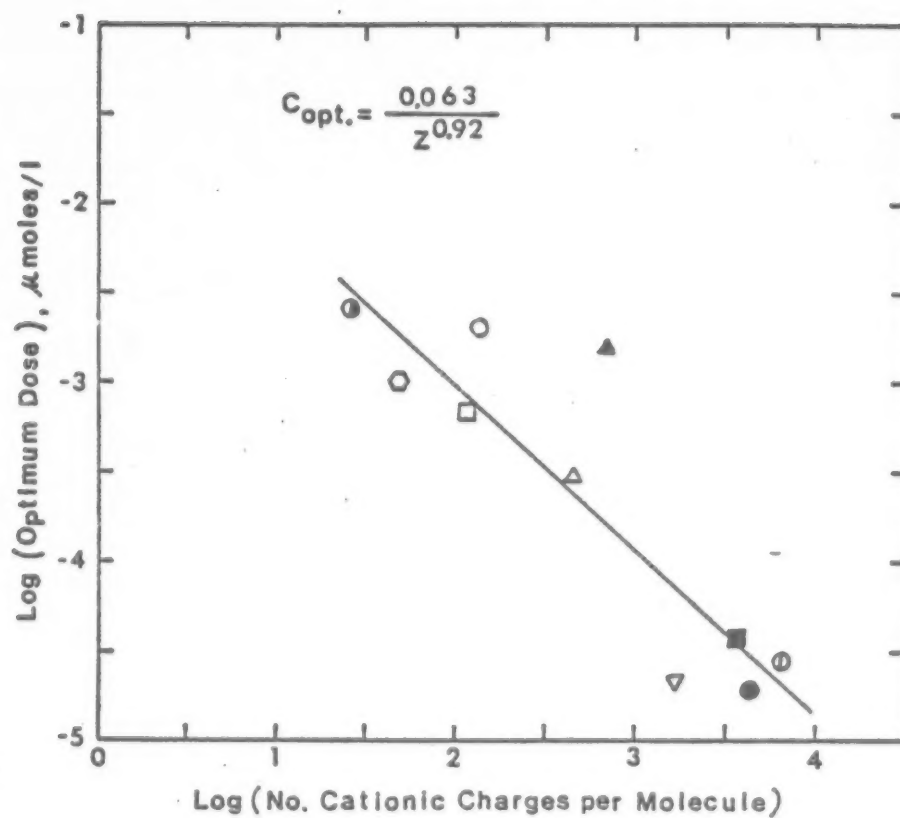


Fig. 32. Relationship Between Optimum Dose and Polymer Charge

Such a relationship indicates that the action of low molecular weight cationic polymers is primarily dependent on charge density per molecule. The differing pH's and size of chain length really mean different net charge per molecule. Good correspondence between electrophoretic mobility and jar tests further attests to this fact. For most low molecular weight polymers, coulombic interactions between colloid and polymer may play a dominant role and bridging, as modelled by LaMer and coworkers (6) (16), plays only a minor role. As proposed by Gregory (41), the adsorption of a charged polymer segment on an oppositely charged surface is much faster than the collision kinetics. Therefore, adsorption and charge neutralization, at the "patches" where polymer is adsorbed, is essentially complete before particle aggregation begins. The patch charge may be assumed to be equal to the algebraic sum of the number of charges on the polymer molecule and the number of opposite charges on the "patch" of the colloid surface covered by the polymer molecule (14). The data presented in Table 10 show that the concentration of polymer needed to initiate flocculation (ccc) does not depend on $\langle M \rangle_n$ or the amount of polymer adsorbed, Γ_m . The maximum adsorption is perhaps dependent on the electrostatic interactions between molecules of the polymer and space requirement of the polymer molecule. The lack of agreement between θ_{opt} of 50% predicted by La Mer and the θ_{opt} values presented in Table 10 also suggests that polymer bridging is perhaps not the major mechanism of polymer-particle interactions investigated in the present work.

The selection of polymer for direct filtration should be based primarily on the cationic charge density per molecule. Preferably, low molecular weight polymers should be used. The optimum dosage may be determined from rapid-mix test (at $G=650 \text{ sec}^{-1}$ for 3 minutes) followed by

particle size analysis. The use of a slow mixing period in determining dosage for direct filtration is not warranted in most cases. The objective of polymer use in direct filtration is not to promote flocculation preceding filtration. In order to obtain longer filter run, uniform use of the entire bed depth by deeper penetration of particulates into the bed should be promoted. This can be done by using polymer doses somewhat less than optimum as determined from jar tests.

I. Direct Filtration Studies

The purpose of the studies on direct filtration was to investigate how well the dosages, mixing intensities, and durations could be selected from coagulation studies described in sections A through H of this chapter. Results will be presented for filter runs performed on a single media sand filters, 1 inch diameter and 6 inch deep, with sand having an effective size and uniformity coefficient of 0.5 mm and 1.2, respectively, and a bed porosity of 42 percent. In this phase of research, many different polymers were investigated. However, the results from only three different cationic polymers, namely Corcat P-145 ($\langle M \rangle_n = 4 \times 10^4$), Betz 1190 ($\langle M \rangle_n = 5 \times 10^4$), and Betz 1160 ($\langle M \rangle_n = 3 \times 10^6$) have been included in this report. All experiments included in the report were conducted at a filtration rate of 3.5 gpm/sf. However, experiments at 2 and 2.5 gpm/sf, not included in this report were also conducted. The G for polymer mixing were 650 sec^{-1} although, in limited experimentation, the effect of other mixing intensities were also investigated. The mixing duration was 3 minutes for most filter runs. However, the results from a longer duration of mixing have also been presented. The effect of polymer dosages, at optimum levels selected from flocculation studies (particle counting), and at suboptimum and super optimum dosages as well, on the filtration of bentonite suspensions, have been included. The filter performance was described both in terms of effluent quality, turbidity, particle size, and headloss during clogging.

Experiments were also conducted using dual media anthracite-sand filters. A 3-inch diameter filter column with 20 inches of anthracite (effective size = 1 mm, uniformity coefficient = 1.4 and porosity 0.52) overlying 12 inches of sand of same characteristics as that of the aforementioned single media filter was used. Some results from dual media filtration studies with mixed metal hydroxide suspensions have been presented in this report. It should be noted that polymer mixing at various G's preceding filtration was provided in a specially designed mixing vessel equipped with either a 1 or 4 blade rotor assembly. Tracer studies indicated that the mixing unit provided about 70 percent of the theoretical

detention at different flow rates while operating as an ideal backmix reactor. The actual detention time in the vessel could be varied from 3 to 14 minutes by varying the throughput rate.

i. Results from Studies With Corcat P-145

The turbidity and headloss for the filtration of a 20 NTU (75 mg/l) bentonite suspension using 0.05, 0.5, and 5 mg/l of Corcat P-145 have been presented in Figure 33. The polymer was premixed for 14 minutes at $G=650 \text{ sec}^{-1}$. From previous jar tests and particle counts, a dosage of 0.5 mg/l was found to be the optimum for the 20 NTU bentonite suspension when rapid-mixed for 3 minutes at $G = 650 \text{ sec}^{-1}$. However, it was found that at a mixing duration of 3 minutes, optimum dosage for filtration was not 0.5 mg/l for this low molecular weight polymer. Therefore, the premixing time was increased to 14 minutes although the G value remained unchanged. From the effluent turbidity results a stoichiometry between optimum dosage and filtrate quality is obvious as also the correspondence between optimum dosages from jar test and filtration. The typical S-shape of the effluent turbidity curve conforms very well to a classic adsorption-desorption wave front migration phenomenon. As will be demonstrated later, for the high molecular weight polymer Betz 1160, the correspondence between optimum dosages from jar test and filtration for a rapid-mixing duration of 3 minutes was excellent. Apparently, the larger molecular chains, and perhaps branching of polymer chains of Betz 1160, accomplish bridging and/or charge neutralization in a much shorter time. It can also be conjectured that bridging is the dominant mechanism of polymer action for Betz 1160.

a. Analysis of Results of Particle Counts

Figures 34 to 38 present some interesting data for particle counts at various phases of the filter runs described in Figure 33. It should be noted that particle counts only in the size

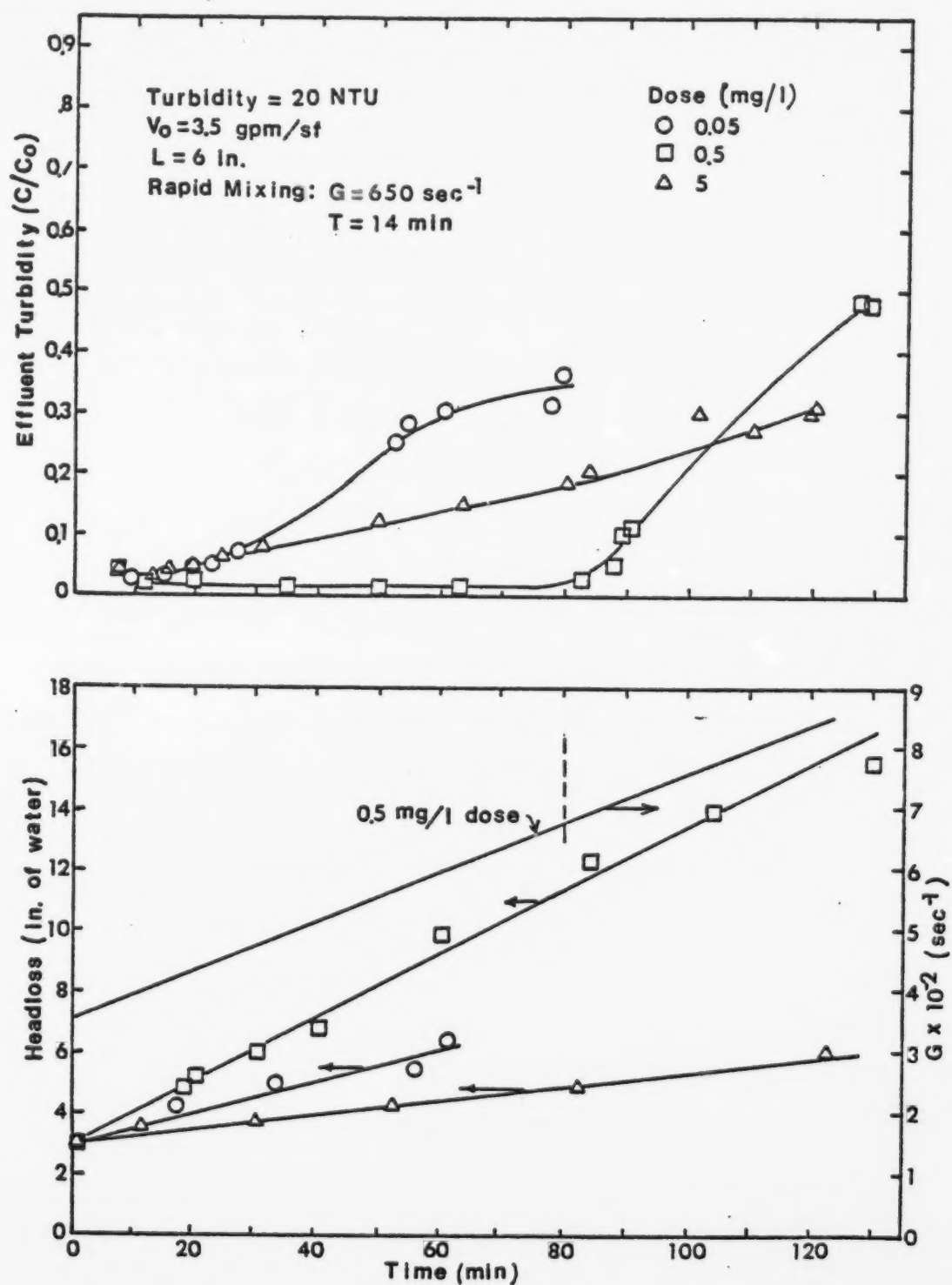


Fig. 33. Effluent Turbidity and Headloss Versus Time (Corcat P-145)

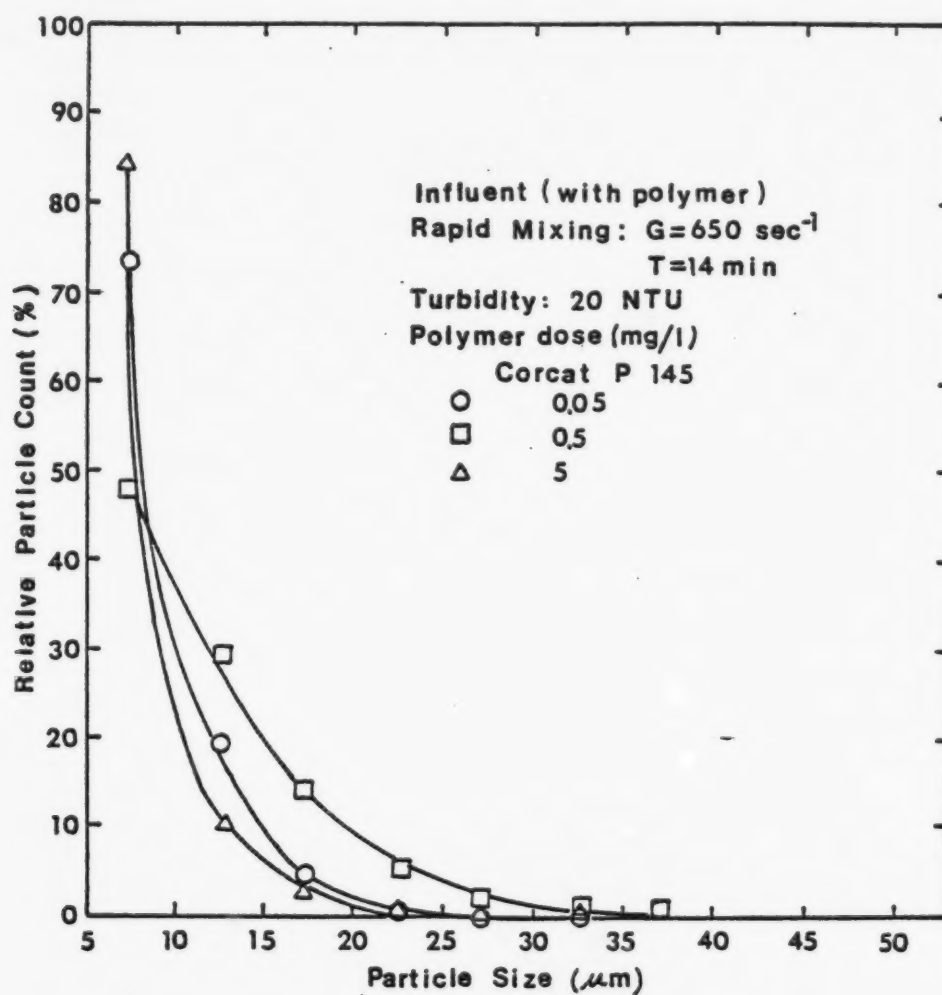


Fig. 34. Particle Size Distribution in Filter Influent After 14-Minute Rapid Mixing at $G = 650 \text{ sec}^{-1}$ (Corcat P-145)

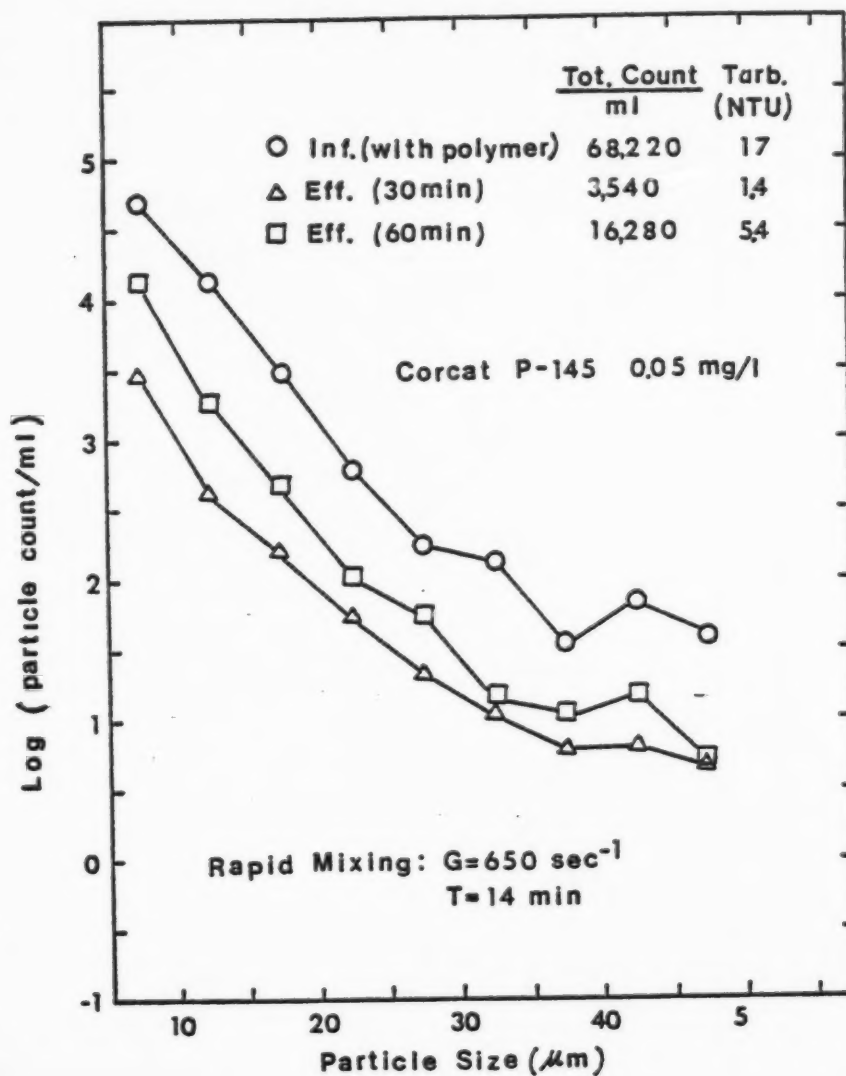


Fig. 35. Particle Size Distribution (Corcat P-145 = 0.05 mg/l)
(refer to Figure 33)

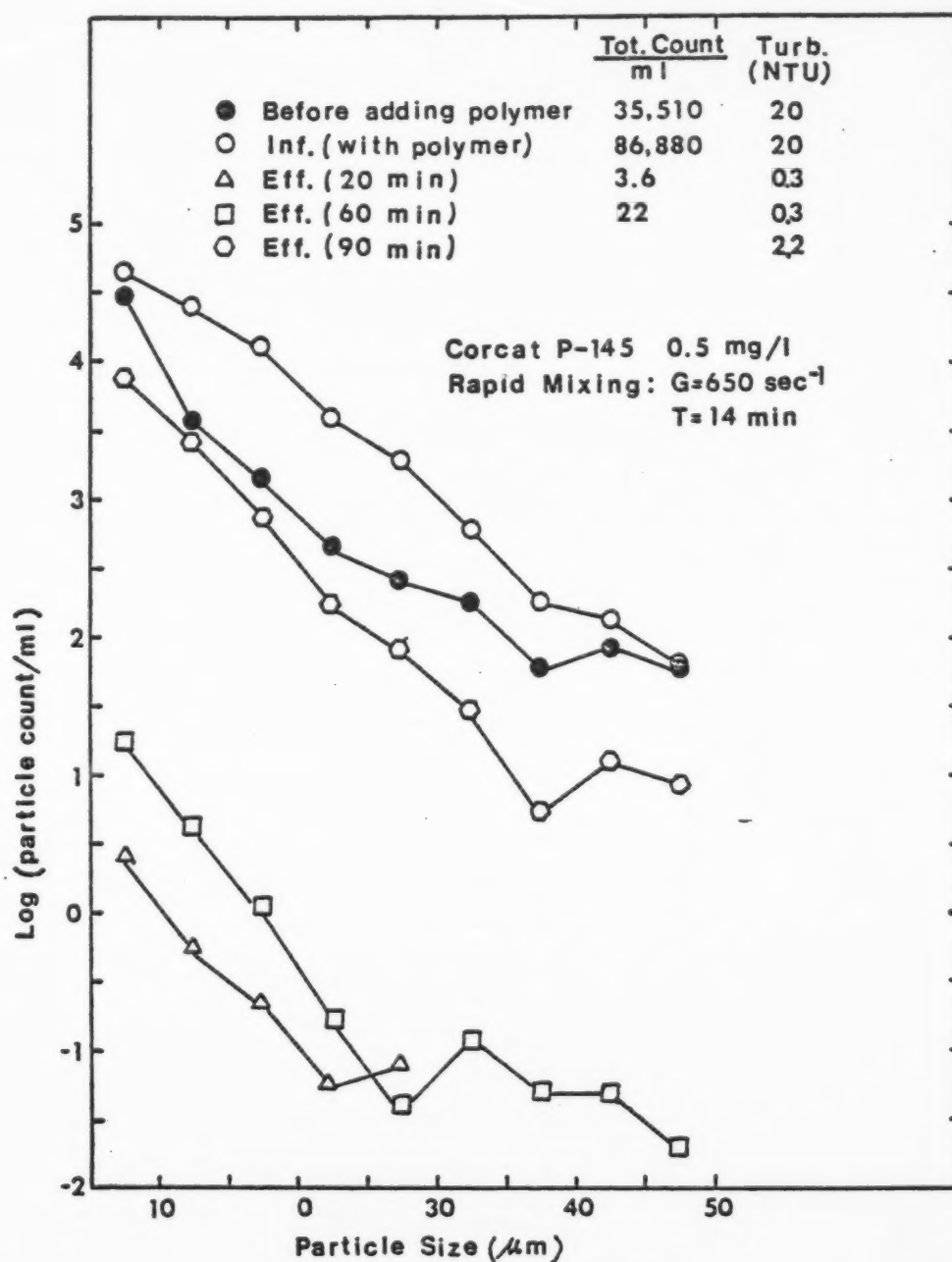


Fig. 36. Particle Size Distribution (Corcat P-145 = 0.5 mg/l)
(refer to Figure 33)

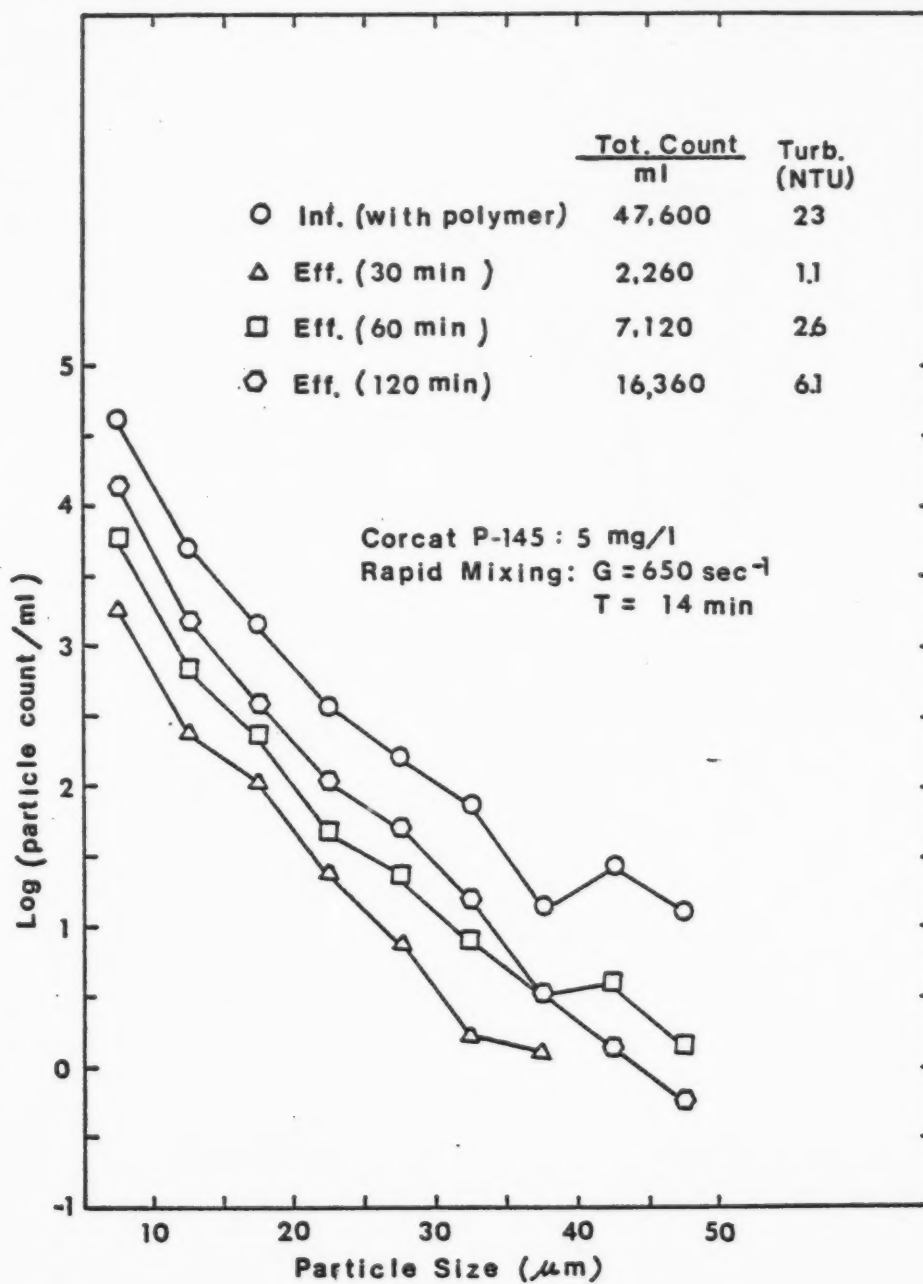


Fig. 37. Particle Size Distribution (Corcat P-145 = 5 mg/l)
(refer to Figure 33)

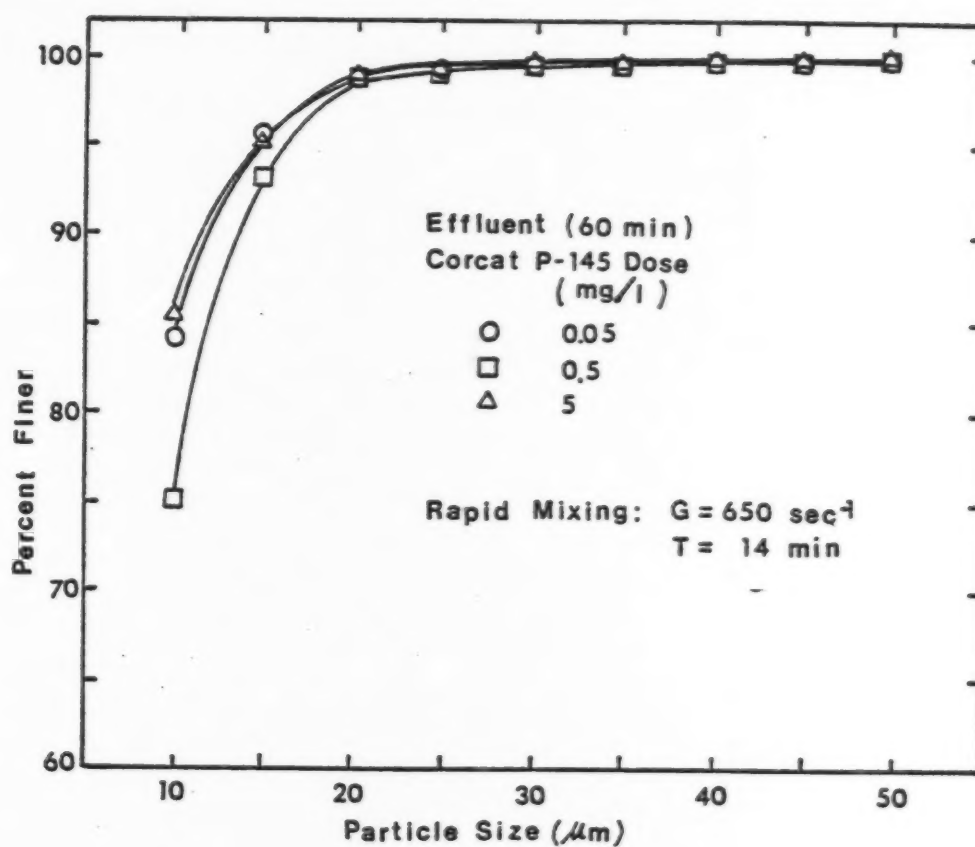


Fig. 38. Cumulative Size Distribution of Particles in Filter Effluent at 60 Minutes and Various Polymer Dosages (refer to Figure 33)

range of 5 to 300 microns have been included. The HIAC sensor used for all counting reported operated only in this size range. The actual counts could conceivably be much higher, especially with under or overdosing of polymers, if particles with less than 5 micron size could be accounted for.

Figure 34 shows relative counts of various size particles following rapid mixing of various dosages of Corcat P-145 with 20 NTU bentonite suspension. Although the difference in fractional counts were not statistically significant, the actual counts of various sizes were very different at these dosages, as can be seen in Figures 35 to 37. For example, the total counts per ml after rapid mixing were 68, 220, 86, 880 and 47,600 at polymer dosages of 0.05, 0.5, and 5 mg/l, respectively, and the corresponding turbidities were 17, 20 and 23 NTU. Figure 35 shows particle count data for influent and effluent at different filtration times for a dosage of 0.05 mg/l. Comparing effluent counts at 60 and 30 minutes, the gradual deterioration of effluent quality becomes obvious although the effluent turbidities did not increase considerably, 1.4 and 5.4 NTU at 30 and 60 minutes, respectively. It is unfortunate that no sample collected between 0 to 20 minutes of filtration was analyzed for particle counts for the 0.05 mg/l dosage. Similar particle count data for dosages 0.5 mg/l (optimum) and 5 mg/l are presented in Figures 36 and 37, respectively. It is interesting to note that, at the optimum dosage of 0.5 mg/l, the particle counts in all size intervals were higher than any other non-optimum dosages, as shown in Figure 34. In fact, Figure 36 indicates that particle counts increased after coagulation at the optimum dosage. This apparent anomaly can be resolved easily if one considers that the numerous original particles of size less than 5

microns, not detected by the sensor, were in fact flocculated and grew to higher sizes and were counted. Hence, the apparent higher counts of particles in all size intervals higher than 5 microns, as a result of flocculation. Again, gradual deterioration of water quality from the standpoint of particles was indeed striking. The advantage of particle counting over turbidity measurements, especially at low levels of turbidity required of the Safe Drinking Water Act of 1975, is obvious. A quick review of total particle counts and corresponding turbidities observed for filter effluents collected at 20, 60 and 90 minutes at an optimum polymers dosage of 0.5 mg/l (see table in Figure 36) reveals the basic advantage of particle counting. Further, although the turbidity of bentonite suspension remained unchanged at 20 NTU before and after rapid mixing with a polymer dose of 0.5 mg/l, the particle counts increased two and one-half times as a result of flocculation of particles of sizes less than 5 microns into larger, detectable sizes. Figure 38 is a comparison of cumulative distributions of effluent samples collected at 60 minutes during filter runs using 0.05, 0.5 and 5 mg/l of the polymer. No discernable variance was noted in cumulative distributions although the total counts (and counts in different size intervals as well) were 16, 280, 22 and 7,120 per ml at these dosages, a revealing observation indeed.

b. Calculation of G in Clogging Filters

The increase in the number of fine particles in the effluent as a function of time indicated either the possibility of break up of flocs within pore spaces or the erosion of predeposited flocs from the surface of collector sand grains, caused by the increased liquid shear energy in a clogged bed. The G values within the bed were calculated from the following:

$$G = \left(\frac{Q_0 \rho g h}{f V \mu} \right)^{\frac{1}{2}} \quad (25)$$

$$= \left(\frac{V_0 \gamma h}{f L \mu} \right)^{\frac{1}{2}} \quad (26)$$

γ = specific weight of flocs = 62.22 lb/cf @ 27c

h = headloss, ft

V = approach velocity, ft/sec

f = porosity

L = depth of media = 1.5 inches

μ = viscosity = 1.8×10^{-5} lb-sec/sf @ 27c

G = velocity gradient, sec^{-1}

Assuming that most of the headloss increase occurs in the top 1.5 inches of bed, an approach velocity of 3.5 gpm/sf, temperature of 27C, and a porosity of 0.42, Eq. 26 reduces to

$$G = 717 h^{\frac{1}{2}} \quad (27)$$

The calculated values of G at various times of filtration have been plotted in Figure 33 for a filter run using a polymer dosage of 0.5 mg/l. For this run breakthrough occurred at about 80 minutes. Figure 36 indicates a tremendous increase in particle count between the time 60 and 90 minutes, probably due to breakthrough that occurred at 80 minutes. The value of G at $t=80$ min. was 670 sec^{-1} which corresponds to a shear energy of only 6 dyne-cm/cc, equivalent to 3.2×10^{-9} kcal per mole of water, an insignificant energy considering that the energy hydrogen bonding is 5 kcal/mole. Since breakage of flocs occurred at very low energies, apparently the forces holding the flocs together must be very weak.

c. The Effect of Premixing Intensity on Filtration

If one assumes that polymer-induced coagulation and flocculation in direct filters occur within the pore spaces rather than preceding filtration, then a change in G during polymer mixing should not have any influence on filtrate quality or the length of filter run. However, as Figure 39 indicates, a variation in G for a fixed duration of mixing appeared to affect the filtrate quality, that is, the time of breakthrough. The three filter runs depicted in the figure were conducted at a filtration rate of 3.5 gpm/sf in a 6-inch deep, 1-inch diameter column. All filter influents had a turbidity of 20 NTU and received an optimum dosage of 0.5 mg/l of Corcat P-145 mixed for 14 minutes at G 's of 300, 650 and 990 sec^{-1} . Apparently, the initial mixing has an influence on filter performance. The interaction of polymer with particles is irreversible from a charge neutralization and/or polymer bridging hypothesis. However, larger counts or higher turbidity under high mixing could be caused by the shearing of preformed floc to smaller flocs (not original particles) under high mixing conditions, which could never flocculate in the filter. It has already been shown that the filter effluent deteriorated when G in clogged filters became high. Figure 39 shows that it is equally important that an optimum mixing is maintained during dispersion of polymer to insure good filtration. The headlosses at optimum and higher than optimum G 's were identical. The cumulative particle size distribution in filter effluent after 60 minutes of filtration for different polymer mixing conditions are shown in Figure 40. Although the difference between the cumulative distribution is not significant statistically, the difference between total counts of particles was very meaningful. These data suggest that, contrary to

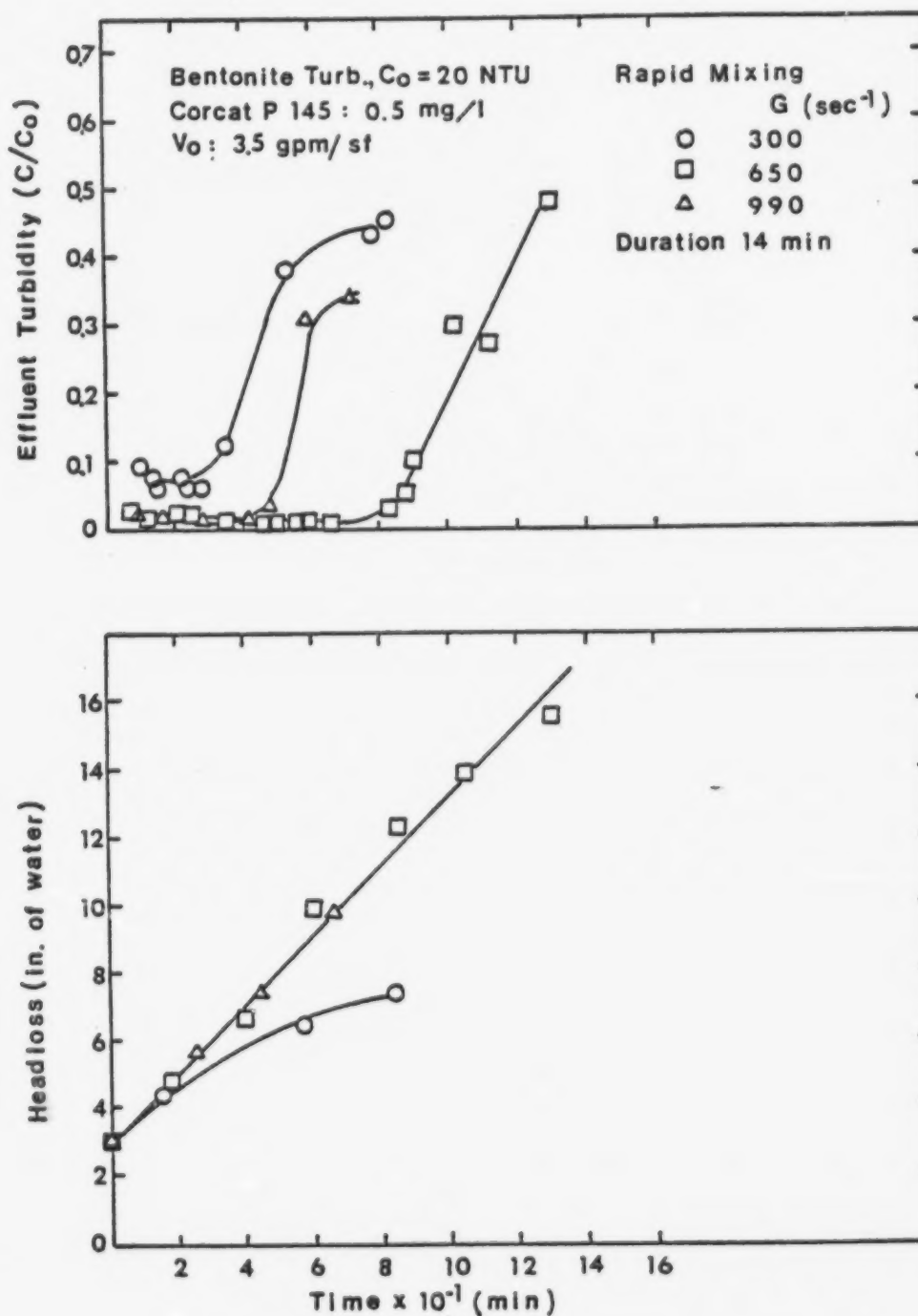


Fig. 39. Effect of Rapid Mixing Intensity on Effluent Quality and Headloss (Corcat P-145)

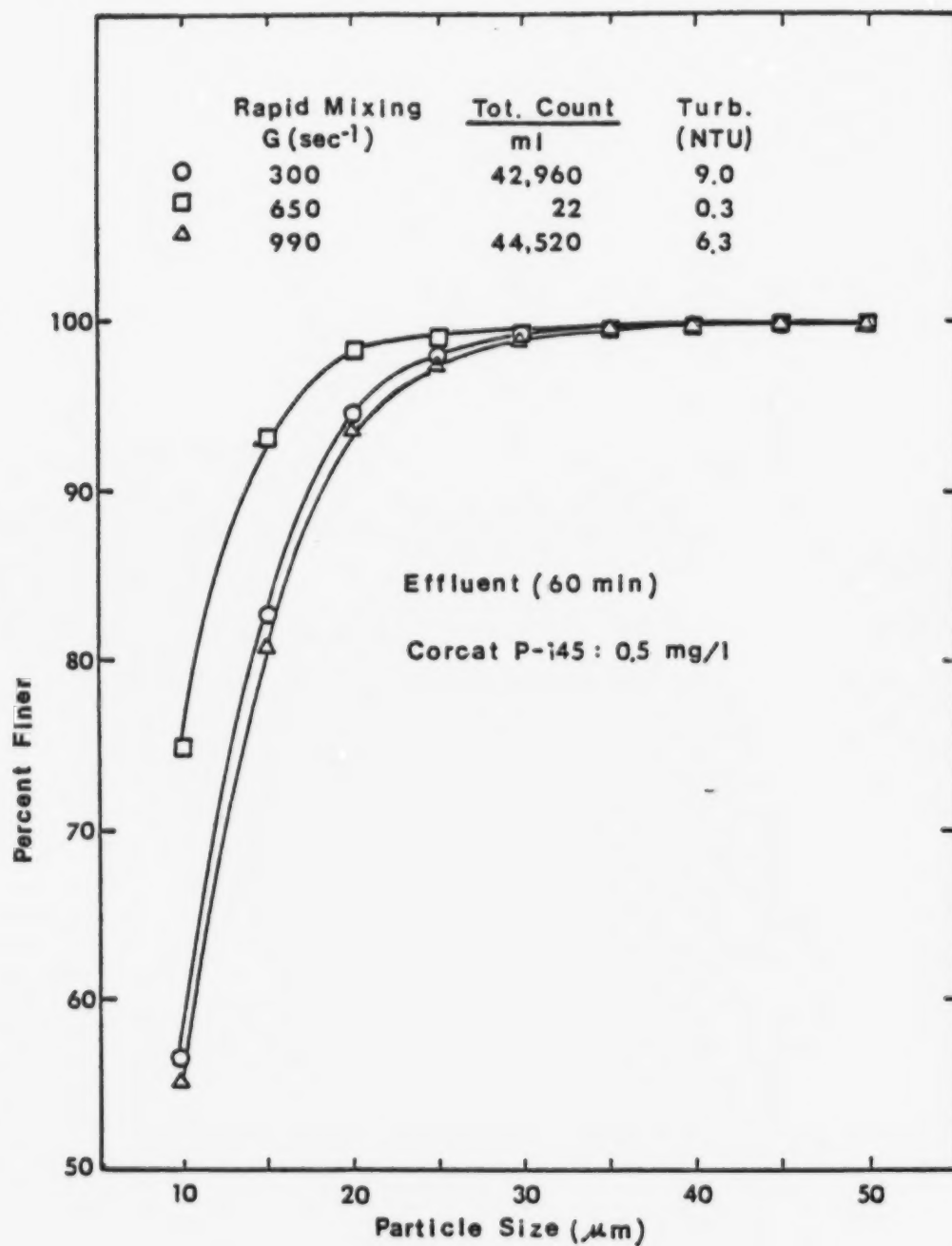


Fig. 40. Particle Size Distribution in Filter Effluent at 60 Minutes Under Different Rapid Mixing Conditions (refer to Figure 38)

common beliefs, polymer-particle interactions and even growth of flocs are essentially complete during rapid mixing, at least for low molecular weight polymers as shown in Figure 22, and essentially similar relative particle distribution is maintained in the effluent as in the influent. If it is accepted that the particle-polymer interaction is irreversible then the mixing conditions and their influence on direct filtration become extremely important. The particle size distribution in filter effluents at various times of filtration at premixing G of 990 and 300 sec^{-1} are presented in Figures 41 and 42, respectively. Both of these runs were made at the optimum polymer dosage of 0.5 mg/l as described in Figure 39. Figures 41 and 42 should be compared with Figure 36 that shows the particle size distribution in filter effluent when a G of 650 sec^{-1} was used for the mixing of polymer while other variables were kept constant. Figures 43 and 44 summarize the results of all filtration experiments performed at different dosages of Corcat P-145 and under different polymer mixing conditions. The duration of mixing was kept constant at 14 minutes for all filter runs. The criteria to measure filter performance were the volume of water processed till a 10 percent breakthrough of turbidity (not particle counts) was reached and also the rate of headloss development. Perhaps total particle counts above a certain cutoff particle size would be a better criterion for measuring effluent quality rather than turbidity, as is commonly used.

ii. Results from Studies with Betz 1190

The molecular weight of Betz 1190, 5×10^4 , is comparable to that of Corcat P-145, 4×10^4 . The charge densities of these polymers, 300 and 260 coulombs/gm for Corcat P-145 and Betz 1190, respectively, are also quite comparable. The optimum dosage at a pH of 8, as determined from jar

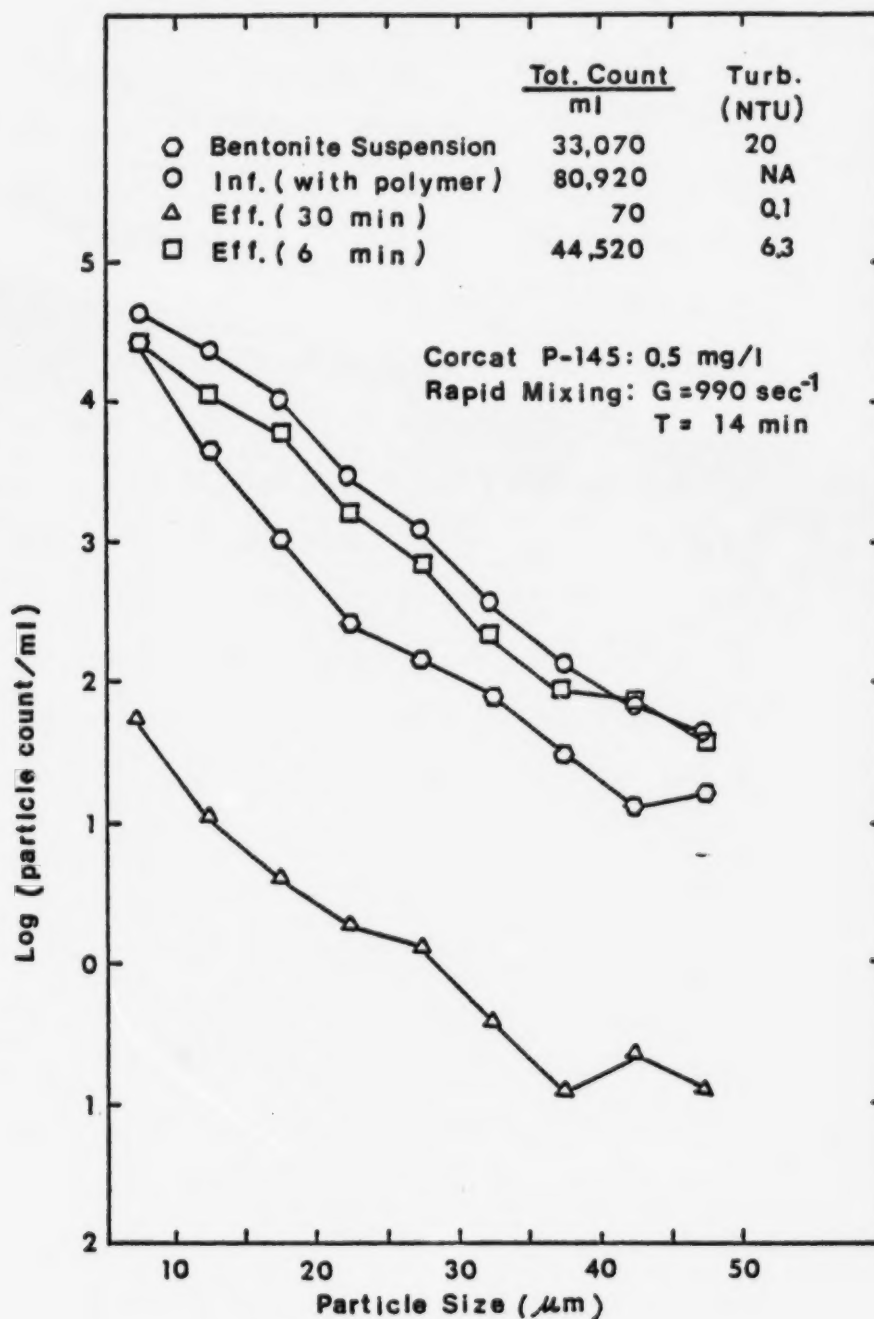


Fig. 41. Particle Size Distribution in Filter Effluent for Mixing at $G = 990 \text{ sec}^{-1}$ (refer to Figure 39)

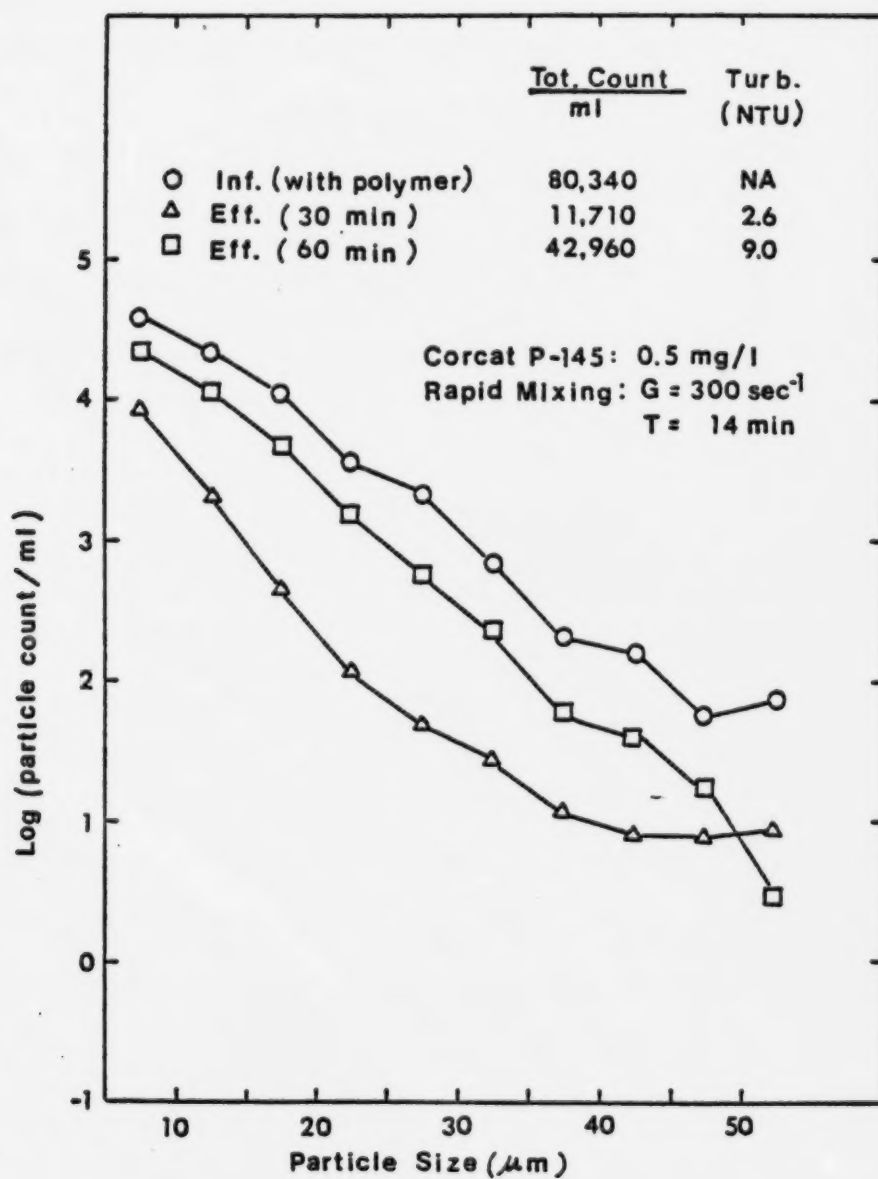


Fig. 42. Particle Size Distribution in Filter Effluent for Mixing at $G = 300 \text{ sec}^{-1}$ (refer to Figure 39)

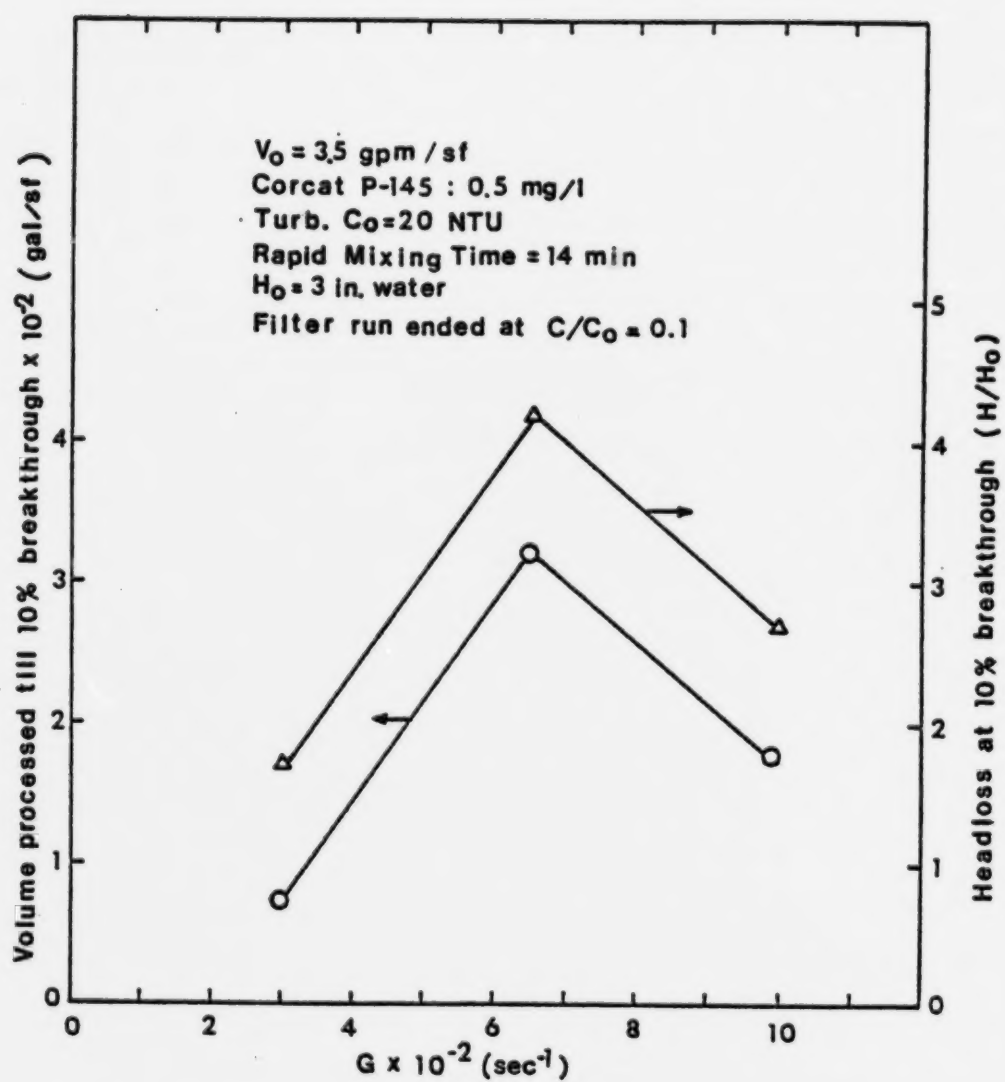


Fig. 43. Influence of G on Duration of Filter Run (Corcat P-145)

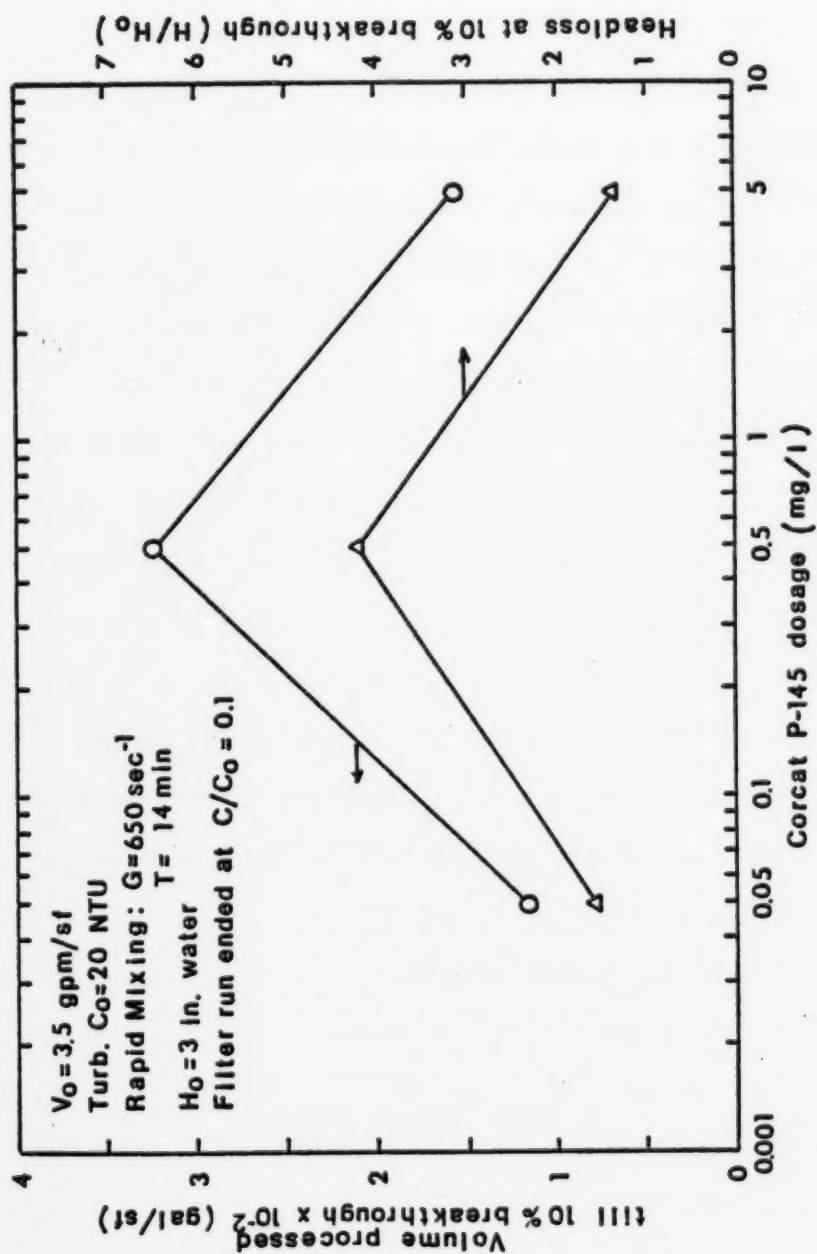


Fig. 44. Duration of Filter Run at Various Dosages of Corcat P-145

tests and particle counts, was 0.5 mg/l and the optimum rapid mixing conditions were found to be a G of 650 sec^{-1} and a duration of mixing of 3 minutes. Figure 45 presents results from filtration for the aforementioned conditions. It can be clearly seen that 0.5 mg/l did not give the best filter performance. Seemingly, 5 mg/l appeared to yield best results. It was felt that a 3-minute mixing period was not sufficient to precondition the bentonite suspension ideally for filtration. Although the interaction of polymer and particle occurs very fast, a certain amount of residence in a dynamic continuous complete-mix reactor may be required to initiate the growth of flocs prior to the entry of the feed to the filter. Figure 46 presents results from exactly similar filter runs but for a duration of mixing of 14 minutes. The optimum dosage for filtration did match with the 0.5 mg/l dosage predicted from jar tests. The rate of headloss increase was somewhat higher when a mixing time of 14 minutes was used. Figure 47 shows a cumulative frequency distribution of particles in filter influent following mixing at $G=650 \text{ sec}^{-1}$, $t=14 \text{ min}$ with optimum, suboptimum, and superoptimum dosages of Betz 1190. Figure 48 shows similar results for influent and effluents collected at 30 and 50 minutes of filtration at an optimum dosage of 0.5 mg/l of Betz 1190 mixed with 20 NTU bentonite at a G and t of 650 sec^{-1} and 14 minutes, respectively. Figures 49 and 50 show the actual numerical counts of particles in various size intervals in the influent and filter effluents for filter runs using an optimum Betz 1190 dosage of 0.5 mg/l, mixed with bentonite suspension at a $G = 650 \text{ sec}^{-1}$, at two different durations of mixing, namely 3 minutes (Figure 49) and 14 minutes (Figure 50). The influent size distributions for 3 and 14-minute mixing times compare favorably. However, the particle counts in the 30-minute effluent samples obtained under two different mixing durations were dramatically different. It does indicate that the rate of floc growth is directly proportional to polymer dosage and that

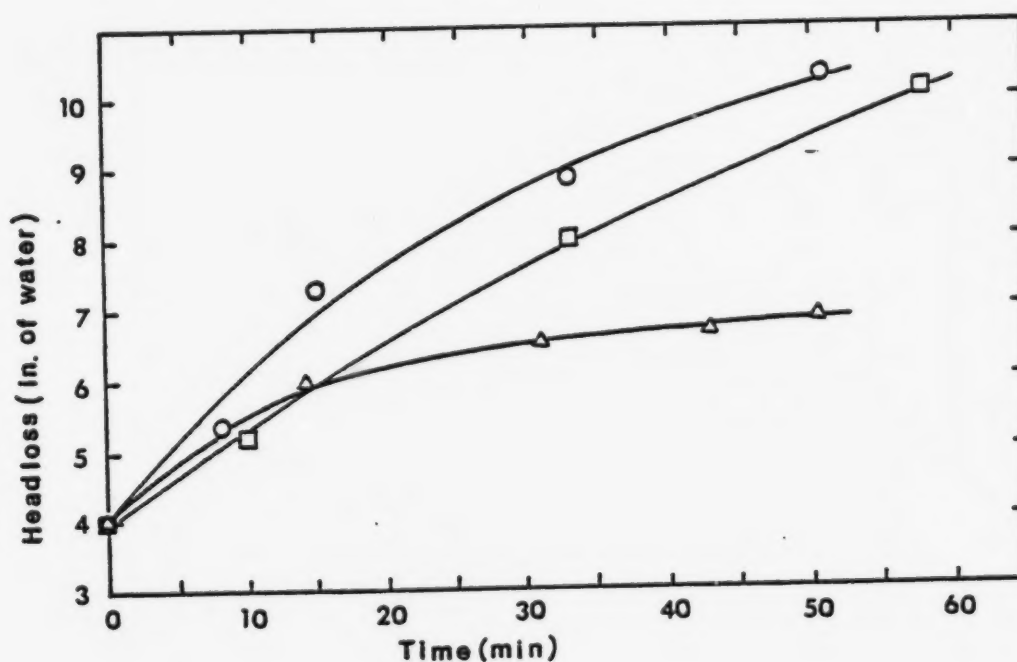
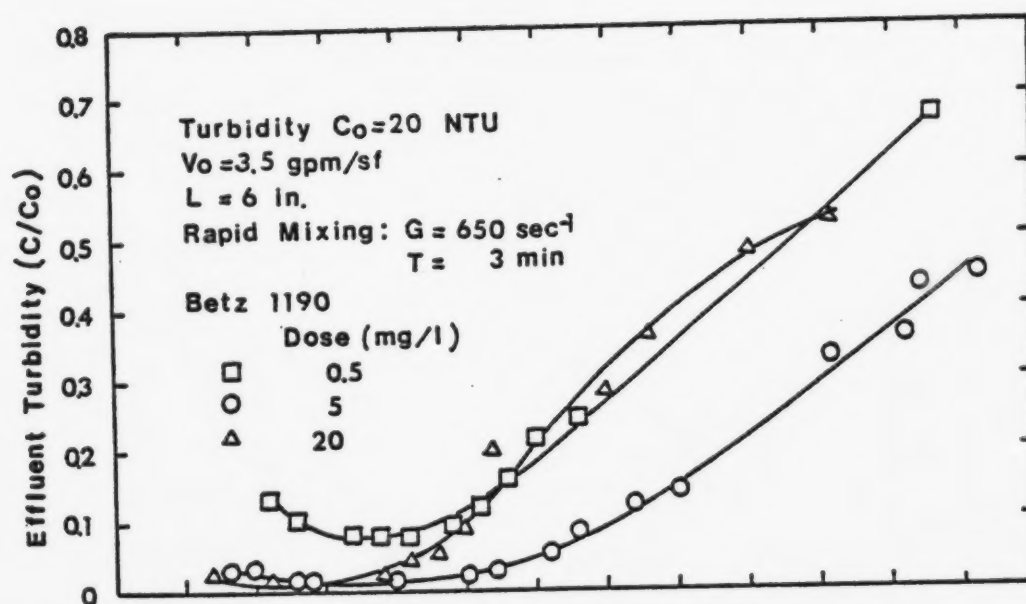


Fig. 45. Effluent Turbidity and Headloss Versus Time
(Betz 1190; Duration of Mixing = 3 min.)

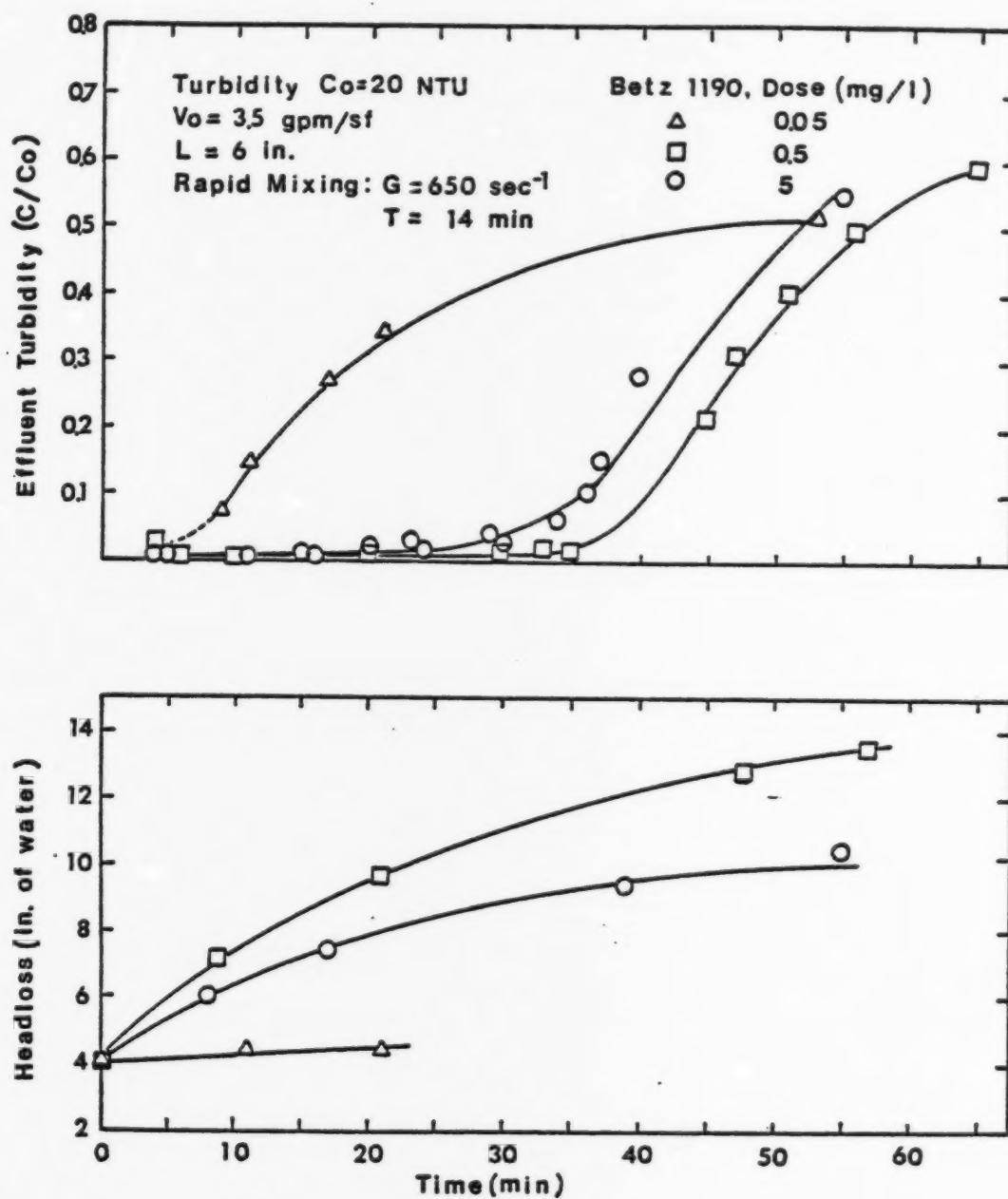


Fig. 46. Effluent Turbidity and Headloss Versus Time (Betz 1190; Duration of Mixing = 14 min.)

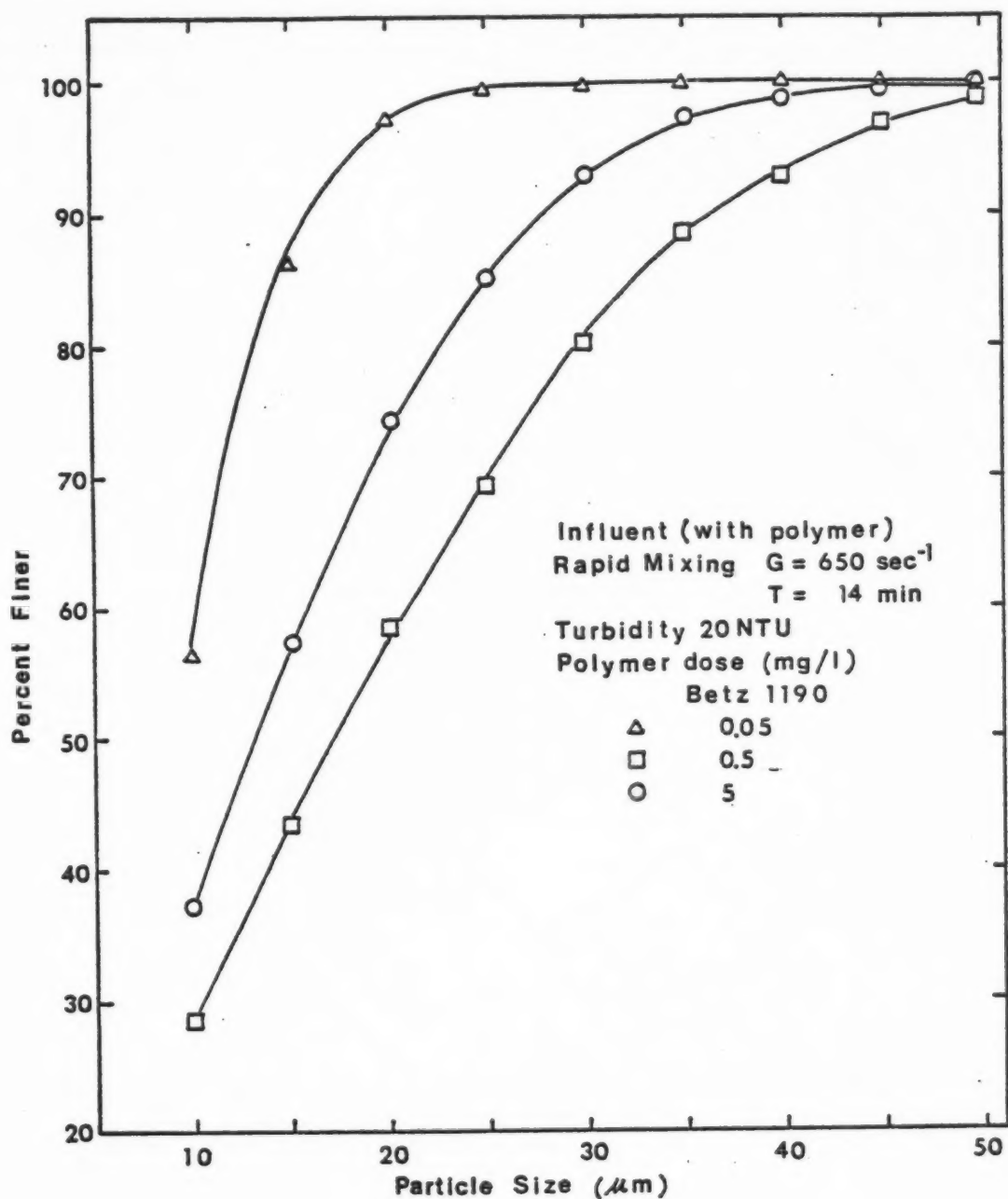


Fig. 47. Particle Distribution in Filter Influent at Various Dosages (Betz 1190)

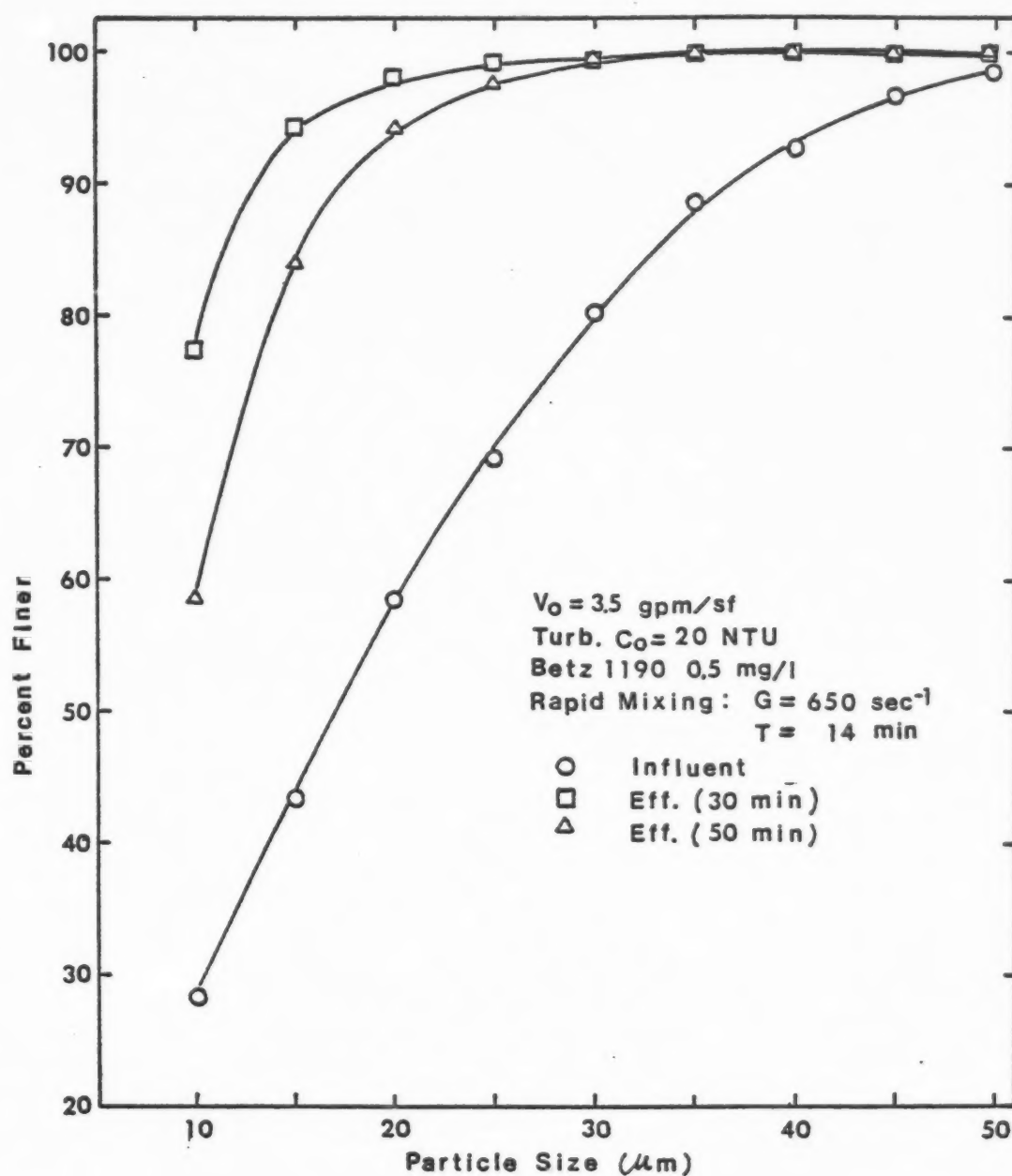


Fig. 48. Particle Size Distribution in Filter Effluent
(Betz 1190 dose = 0.5 mg/l)

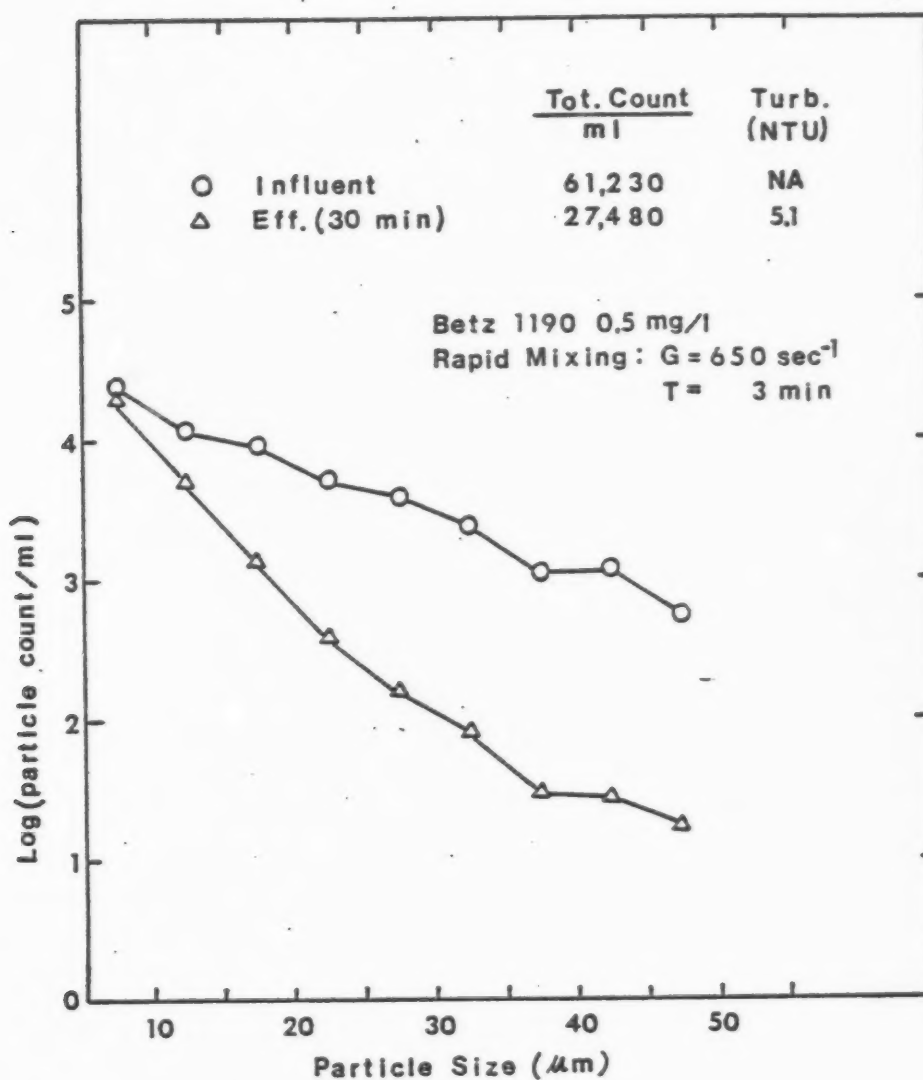


Fig. 49. Particle Counts in Various Size Intervals
 (Betz 1190; Mixing for 3 min. at $G = 650 \text{ sec}^{-1}$)

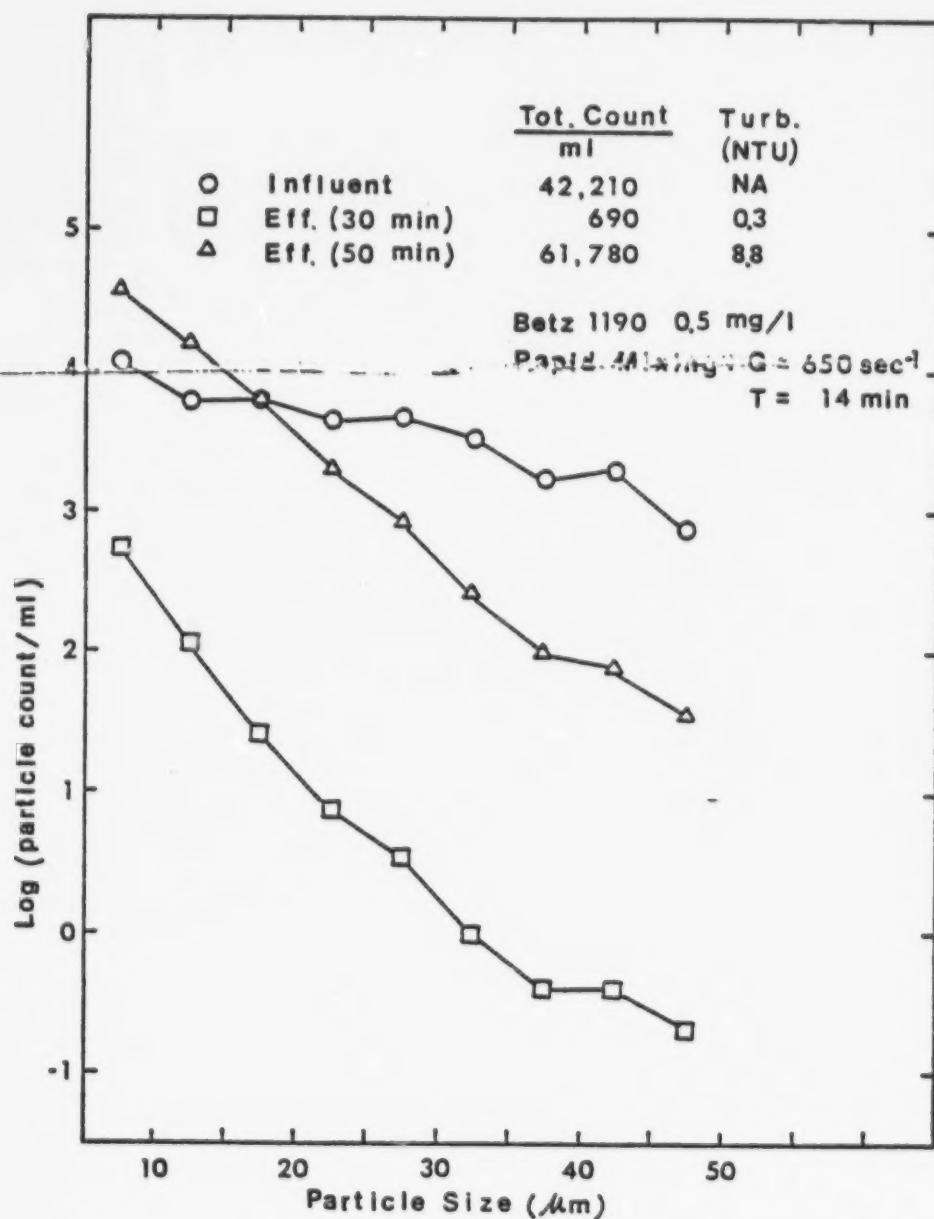


Fig. 50. Particle Counts in Various Size Intervals
 (Betz 1190; Mixing for 14 min. at $G = 650 \text{ sec}^{-1}$)

filter performance depends, in a limited sense, on the rate of floc growth.

iii. Results From Studies With Betz 1160

Only limited filtration experiments were done with Betz 1160, a high molecular weight (3×10^6) cationic polymer. The headloss development with this polymer was extremely rapid. The results of filter runs at different dosages and at two different durations of mixing at $G = 650 \text{ sec}^{-1}$ are shown in Figure 51. From flocculation studies and particle counts, the optimum dosage was predicted as 0.1 mg/l when mixed for 3 minutes at a velocity gradient of 650 sec^{-1} . At this optimum dosage, extremely good effluent quality could be maintained for a long time, but the headloss development was quite high. By increasing the mixing time to 14 minutes, the filtrate quality deteriorated much faster, even at the optimum dosage of 0.1 mg/l. At an underdose of 0.01 mg/l, filtrate quality deteriorated very rapidly and there was no significant headloss because there was little removal of particles. At overdoses ($>1 \text{ mg/l}$), regardless of the duration of mixing, filtrate quality improved quickly initially but then began to deteriorate. Large flocs collected at the top of the filter and the headloss increase indicated the classic shape of septum filtration. No particle count data were collected because it was decided to discontinue further experimentation with such large molecular weight polymers on account of termination of filter runs due to extremely high headloss. It should be noted that, since large molecular weight polymers act mainly through polymer bridging, flocculation studies should accurately predict optimum dosages for direct filtration. Further, flocculation is quite fast and perhaps is complete before the influent enters the filter bed. The bed penetration is very poor and the filter depth is underutilized.

iv. Comparison Between Betz 1190 and Corcat P-145

The filter performance, as measured by volume of water processed and headloss, were compared for these two polymers for ten percent breakthrough

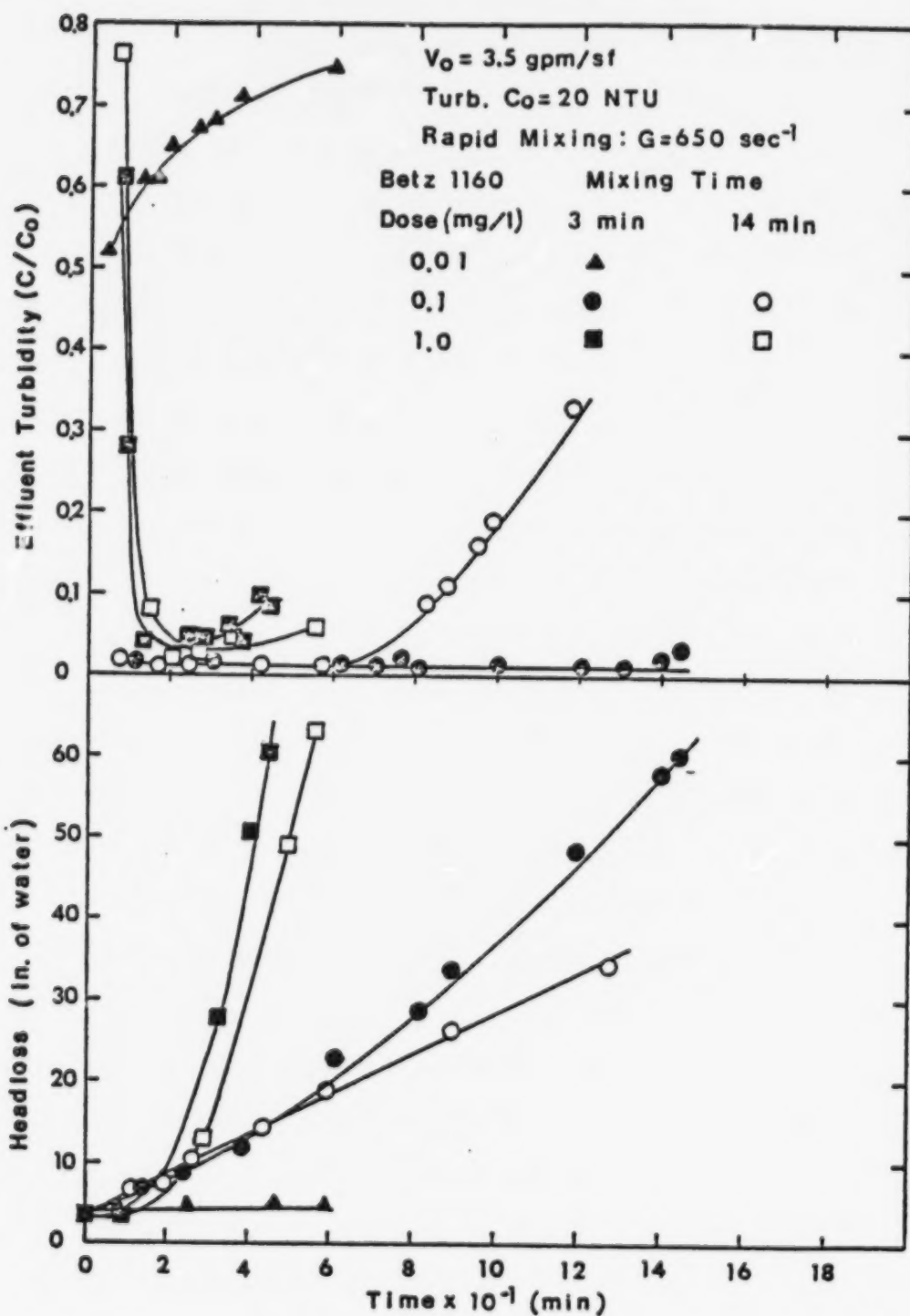


Fig. 51. Effluent Turbidity and Headloss Versus Time (Betz 1160)

and the results are shown in Figure 52. The results of filter runs only at similar dosages and mixing conditions have been included. Corcat P-145 performed considerably better than Betz 1190 at all dosages. The volume of water processed at the optimum dosage was 1.67 times with Corcat than with Betz 1190. However, the increase in headloss for Corcat P-145 was not much higher than for Betz 1190. Corcat P-145 has a somewhat smaller molecular weight and larger charge density than Betz 1190. No definite conclusion can be drawn, but the better performance of Corcat could be attributed to its higher charge density.

v. Dual-Media Filtration of Mixed Metal Hydroxide Suspension

The characteristics of the dual media filter has been presented at the beginning of section I. The stock suspension of mixed metals was prepared by slowly adding 1.0 N NaOH solution to a mixed metal solution containing 1200 mg/l nickel, 240 mg/l of zinc, and 60 mg/l of copper, till a pH of 10.5 was reached. Appropriate dilutions of stock suspensions were made using tap water to give desired turbidities. The final pH of the influent to the filter averaged at 8.4. Results from typical filter runs using Betz 1175, a cationic polymer with a molecular weight only 10,000, are shown in Figure 53. Various combinations of filtration rate and polymer dosage were used. The advantage of using a polymer is clearly demonstrated. For a 10 NTU mixed metal hydroxide suspension being filtered at 2 gpm/sf, 3 mg/l appeared to be the optimum polymer dosage. By doubling the filtration rate, breakthrough of turbidity occurred much sooner. The high headloss was caused by larger mass flux into the filter. Part B of Figure 53 shows particle size distributions for the influent and effluent for a filtration rate of 2 gpm/sf and a polymer dose of 0 and 3 mg/l. The effluent samples were collected before a 10 percent breakthrough occurred. It should be noted that for these studies the polymer was injected directly into the filter without any special mixing arrangement. Conceivably, with proper mixing the optimum dosage would have been less. Table 11 summarizes

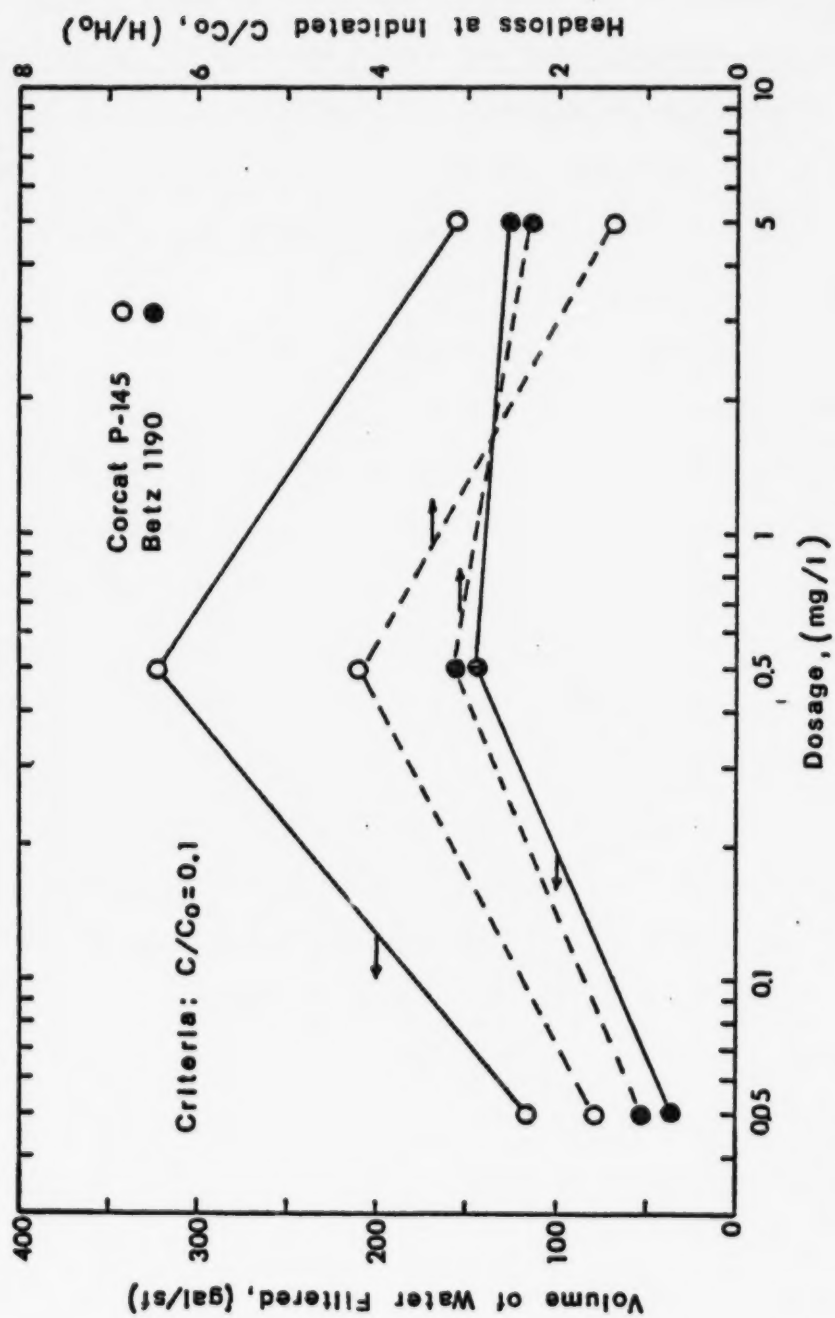


Fig. 52. Comparison of Filter Performance Between Betz 1190 and Corcat P-145

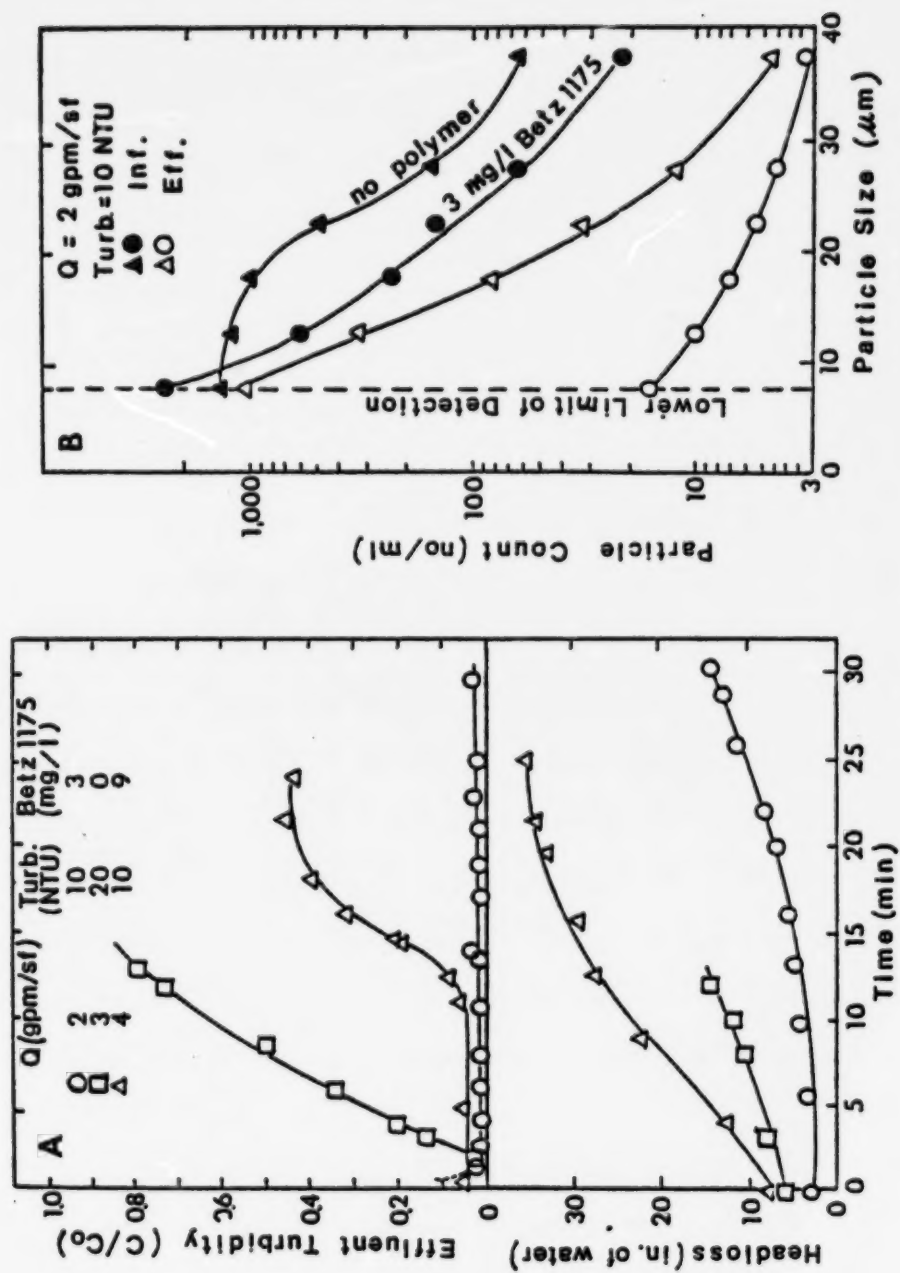


Fig. 53. Filtration of Mixed Metal Hydroxides in Dual Media Filters

Table 11. Filtrate Metal Concentrations in 32-inch Dual Media Deep Filter

Q (gpm/ft ²)	Polymer Applied	Time (hr)	Depth (in.)	Turbidity (NTU)	Total Metal Concentration (mg/l)		
					Ni	Cu	Zn
2	Media precoated with Betz 1175, 0.82 gmpolymer/lb of media No polymer used in the influent	0.30	0	9.8	26.2	1.6	9.2
			32	0.3	7.2	trace	trace
		1.33	0	11	30.7	1.9	9.1
			32	0.3	5.3	trace	trace
		2.25	0	12	28.9	2.9	8.4
			32	0.3	9.5	trace	trace
		4.25	0	11	30.4	1.7	7.6
			32	0.3	6.3	0.3	
4	No precoating of media. Influent Betz 1175, dosage 9 mg/l	0.25	0	7.9	24.3	1.2	6.0
			32	0.3	1.1	trace	0.5
		1.00	0	11	29.6	1.6	7.9
			32	0.3	2.6	trace	0.4
		2.25	0	10	26.0	1.6	8.2
			32	2.0	6.3	0.4	2.0
		3.00	0	9	22.0	1.5	7.3
			32	3.5	9.4	0.7	3.4
		4.00	0	11	18.2	1.7	7.8
			32	5.0	6.2	1.0	4.2

some results from filter runs with mixed metal hydroxides using Betz 1175. Data have been presented for filters that were precoated with polymers but with no continuous feed and also for filter runs where no precoating was used. Analyses of metals in the influent and in the effluents at various times during filtration indicate satisfactory removals in the 32-in filter during the 4-hr. period the samples were collected.

vi Kinetic Aspect of Polymer Adsorption

In selecting dosages for direct filtration, especially for high molecular weight polymers, it is extremely important to consider the rate of adsorption of polymer on colloid surfaces. Rate of flocculation is an important consideration in selecting dosages where the ultimate goal is separation of particulates by flocculation and settling. When polymer is added, several processes begin:

1. Mixing of polymer molecules among the particles
2. Diffusion of polymer and attachment to particles by adsorption
3. Reformation or rearrangement to attain an equilibrium configuration.
4. Collisions between coated particles leading to the growth of flocs.

In preconditioning particles for direct filtration using polymers, the first three processes above are important. The main objective is to create high enough turbulence, G in the range of 300 to 600 sec^{-1} depending upon the molecular weight, for a short period, 3 to 8 minutes, and to discourage any significant floc growth before filtration. It can be assumed that the first process is instantaneous. The second process, adsorption, is dependent on the concentrations of colloid surface and polymer

$$-\frac{dc}{dt} = kcn \quad (28)$$

where c is polymer concentration and n , numerical concentration of colloids. Assuming n to be constant

$$\ln (c_0/c) = k c_0 t \quad (29)$$

It is reasonable to assume that a certain fraction of polymer, x , must be adsorbed before bridging would occur. The time to adsorb this fraction is

$$t = - [\ln (1-x)] / k c_0 \quad (30)$$

this time should be compared with the flocculation time t_f , the time interval between two collisions. Assuming k_f to be the flocculation rate,

$$t_f = 1/k_f c_0 \quad (31)$$

$$t/t_f = - [\ln (1-x)] k_f/k \quad (32)$$

Assuming 50% coverage ($x=0.5$) and roughly equal sizes for the polymer molecule and the colloid particle, it can be shown that

$$t/t_f = 0.7 \quad (33)$$

For dissimilar sizes of colloid and the polymer molecule, t should be even smaller. Although no data exist on reformation, the third process mentioned above, it seems more likely to have adsorbed polymers in an extended segment, a non-equilibrium configuration permitting adsorption, then the flatter stable configuration. In fact, such "non-equilibrium" flocculation may be quite common in water treatment practice. In flocculation, it is extremely important to ensure sufficient collisions, to take advantage of this non-equilibrium stage in the polymer-particle inter-

action. In most waters, n is sufficiently high to permit enough collision leading to floc growth in the time needed to reach the equilibrium configuration (reconformation) of polymer molecules. Once the equilibrium is reached, floc break up caused by prolonged high shear will not permit reformation of flocs even when shear is removed, since the polymer had already assumed a flat configuration, not conducive to bridging.

Chapter 5

SUMMARY AND CONCLUSIONS

Polymers found to be good flocculants and also good as aids for direct filtration are nearly always linear homopolymers. Most of these polymers have ionizable groups along the polymeric chain and hence acts as polyelectrolytes. Polyacrylamides and their derivatives are used most commonly as high molecular weight nonionic polymers and are not particularly suitable for direct filtration. A cationic monomer and acrylamide could be copolymerized to give a cationic polyelectrolyte. The other common cationic polymers used in water treatment are polyamides, polyethylenimines (PEI) and polydiallyldimethylammonium chloride (PDADMA). In selecting polymers for potable water treatment care must be taken against their possible toxicity. Traces of monomers occasionally present may cause some problems.

Proper characterization of polymers, including degree of-hydrolysis, rate of solution and intrinsic viscosity is essential, if their mode of action is to be understood. The size and shape of polymer molecules in solution is of considerable interest from the standpoint of their use in flocculation and/or filtration. Light scattering and viscosity measurements, although subject to some uncertainty, are commonly used to determine molecular weight of polymers in solution. Ionic strength of the water may affect the viscosity and the mode of action of polymer considerably. At low ionic strengths the polymer assumes an extended coil configuration and may be ideally suited to form bridges spanning the repulsive double layers of colloids. A practical problem with high molecular weight polymers is the difficulty in dissolving them and the effect of "aging" on polymer chains. In order to achieve complete dissolution of polymers, vigorous agitation may be necessary. But this may cause scission of polymer chains into smaller units.

The method to be used for the determination of optimum dosage depends pri-

marily on the molecular weight and charge characteristics of polymers. Bridging seems to be the major mechanism of flocculation for most anionic and nonionic polymers. Further, very high molecular weight polymers tend to indicate that bridging is the principal mode of their action. Flocculation of particles by polymers of like charge always requires the presence of dissolved salts. For anionic polymers being used to flocculate clay, for example, divalent calcium may be used. Without the presence of such counter ions no adsorption of polymer may occur on the colloid surface. For polymers working via bridging, refiltration may be the ideal method for determining dosages. ~~One of the disadvantages~~ of this method is the need for high colloid concentration for the formation of the cake. But there is a linear stoichiometry between polymer dosage and colloid surface concentration and, therefore, extrapolation of refiltration results to smaller colloid concentrations seems possible. The optimum dosage for "bridging flocculation" is consistent with the fact that the particle surface should be only partly covered with adsorbed polymers, so that attachments with segments from other particles can be formed. At excessive polymer dosages, colloid surfaces become instantly saturated with adsorbed polymer and the particles are restabilized. Bridging is prevented and further, the particles are sterically stabilized. The optimal fractional coverage of colloid surface is 50 percent according to LaMer's quantitative model for bridging.

Polyelectrolytes always interact strongly with surfaces of opposite charge and are quantitatively adsorbed, at least up to the point of charge neutralization. Measurement of electrokinetic potential, particle counts and/or turbidity seem to be ideal methods for determining the optimum dosage of polymer for flocculation and/or direct filtration. Restabilization in such interactions may simply be a result of charge reversal rather than colloid surface saturation by adsorbed polymer. Because of strong electrostatic interaction, polyelectrolyte chains may adopt a rather flat configuration on the oppositely charged colloid surfaces, reducing the possibility of bridging. For this type of polymer-particle interactions, if flocculation is observed to occur at high

zeta potentials before attaining charge neutralization, this may be due to bridging through repulsive barriers. For flocculation to occur via the charge neutralization mode, the charge density per molecule of the polyelectrolyte becomes extremely important.

With high molecular weight polymers, two other important effects, namely an increased rate of flocculation and a wider range of polymer concentration in which effective flocculation may occur, must be noted. The rate decreases but the "flocculation region" widens as the ionic strength is increased. This cannot be accounted for either the electrostatic neutralization or bridging models. The so-called "electrostatic patch" model explains such a behavior of these polymers.

The effect of mixing on dosage of polymer and the filter performance is well documented. Since adsorption process has to overcome a diffusion barrier, rapid mixing for a short period must precede filtration. However, this should not be continued for a period longer than what is absolutely necessary. The polymer segments may be sheared, thus impairing potential flocculation within the filter pores. For most polymers used in water treatment, a rapid mixing at a G in the range of 300 to 650 sec^{-1} for 3 to 8 minutes appears to be sufficient.

Based on the present study, the following major conclusions were drawn:

1. Cationic polymers of low molecular weights, not more than 40,000 to 50,000, and high charge densities per molecule are best suited for direct filtration.
2. Charge neutralization appears to be the major mode of particle destabilization in using a polymer with a charge opposite to that on the polymer. Thus, electrophoretic mobility coupled with measurement of particle counts following rapid mixing will give the most accurate prediction of optimum polymer dosage for direct filtration. These dosages are somewhat higher than that predicted from residual turbidity measurements. To determine dosages for flocculation, jar tests using turbidity measurements seem to be adequate unless one is interested in determining the distribution of particles in the residual turbidity.

3. Rapid mixing at $G=650 \text{ sec}^{-1}$ was found to be sufficient for optimum filter runs. However, the required duration of rapid mixing for small molecular weight polymers appeared to be higher for the 3 minutes predicted from jar tests and particle counting. For large molecular weight polymers, 3 minutes rapid mixing was sufficient.
4. High molecular weight polymers yielded good quality effluent but at the expense of excessive headloss. Therefore, these polymers are not ideally suited for direct filtration.

APPLICATION OF RESEARCH RESULTS:

Water treatment plant operators will be the primary beneficiary of this research. The research provides a rational method for selecting polymers and polymer doses for contact filters. A scientific basis has been provided for the rational design of filtration for polymer-conditioned particulates which would be of interest to designers and consultants.

PUBLICATIONS AND PRESENTATIONS:

1. "Selection and Use of Polymers in Direct Filtration" by M.M Ghosh and H.H. Yeh, for presentation at the Annual Meeting of the American Water Works Association in Atlanta, Ga in June 1980.

2. "Filtration of Metal Hydroxide Suspensions in Dual Media Filters", H.H. Yeh and M.M. Ghosh, for presentation at the National Conference for Environmental Engineers, American Society of Civil Engineers, in New York, July 1980.

TRAINING ACCOMPLISHED:

The project has provided partial support for one Ph.D. student, namely Hsuan-Hsien Yeh. Mr. Yeh is completing a dissertation research on direct filtration. Additionally, partial support was provided to Kristin Mattenson, M.S. student in Civil Engineering, who received training in different experimental methodology used in filtration research. He has applied his training to a study of intermittent sand filtration of washrack wastes sponsored by the U.S. Department of the Army.

REFERENCE CITED

- 1) Hunter, R.J., and Alexander, A.E., "Surface Properties and Flow Behavior of Kaolinite, Part III: Flow of Kaolinite Sols Through Silica Column", J. Colloid Sci., 18: 846 (1963)
- 2) Conley, W.R., and Pitman, R.W., "Innovations in Water Clarifications", Journ. Amer. Water Works Assoc., 52: 1319 (1960).
- 3) Adin, A., and Rehban, M., "High Rate Contact Flocculation-Filtration with Polyelectrolytes", Jour. Amer. Water Works Assoc., 66: 109 (1974).
- 4) Jenckel, E., and Rumbach, B., "The Adsorption of High Molecular Weight Materials from Solution", Zeitschrift Electrochemie, 55: 612 (1951).
- 5) Simha, R., Frisch, H.L., and Eirich, F.R., "The Adsorption of Flexible Macromolecules", Jour. Phys. Chem. 58: 507 (1953).
- 6) La Mer, V.K. and Healey, T.W., "Adsorption-Flocculation Reactions of Macromolecules at the Solid-Liquid Interface", Rev. Pure & Applied Chem., 13, 112 (1963).
- 7) Camp, T.R., "Floc Volume Concentration", Jour. Amer. Water Works Assoc., 60: 656 (1968).
- 8) Morrow, J.J., and Rausch, E.G., "Colloid Destabilization with Cationic Polyelectrolytes", Jour. Amer. Water Works Assoc., 66: 646 (1974).
- 9) Letterman, R.D., et al., "Influence of Rapid Mix Parameters on Flocculation", Jour. Amer. Water Works Assoc., 65: 716 (1973).
- 10) Toei, K., and Kohara, J., "A Conductimetric Method for Colloid Titrations", Analytica Chimica Acta, 83: 59 (1976).
- 11) Toei, K., and Sawada, M., "A Turbidimetric Method for Colloid Titrations", Analytica Chimica Acta, 89: 383 (1977).
- 12) Kawamura, S., and Hannah, G.P., Jr., "Coagulant Dosage Control by Colloid Titration Technique", Proc. 21st Industrial Waste Conf., Purdue University, 381-400 (1966).
- 13) Wnek, W.J., and Davies, R., "An Analysis of the Dependence of the Zeta Potential and Surface Charge on Surfactant Concentration, Ionic Strength, and pH", Jour. Colloid and Interface Sci., 60: 2: 361 (1977).
- 14) Lindquist, G.M. and Stratton, R.A., "The Role of Polyelectrolyte Charge Density and Molecular Weight on the Adsorption and Flocculation of Colloidal Silica with Polyethylenimine", Jour. Colloid & Interface Sci., 55: 1: 45 (1976).
- 15) Stromberg, R.R., Adsorption of Polymers, in "Treatise on Adhesion and Adhesives", Vol. 1, Dekker, NY (1976).
- 16) Smellie, R.H., and La Mer, V.K., "Flocculation, Subsidence, and Filtration of Phosphate Slimes, VI: A Quantitative Theory of Filtration of Flocculated Suspensions", Jour. Colloid Sci., 13: 589 (1958).

- 17) Tomi, D. and Bagster, D.F., "A Model of Floc Strength Under Hydrodynamic Forces", Chem. Engr. Sci., 30: 269 (1975).
- 18) Smith, D.K.W., and Kitchner, J.A., "The Strength of Aggregated Formed in Flocculation", Chem. Engr. Sci., 33: 1631 (1978).
- 19) Letterman, R.D. et al., "Influence of Rapid Mix Parameters on Flocculation", Jour. Amer. Water Works Assoc., 65: 716 (1973).
- 20) Adin, A. and Rebhun, M., "High Rate Contact Flocculation-Filtration With Cationic Polyelectrolytes", Jour. Amer. Water Works Assoc., 66: 109 (1974).
- 21) Shea, T.G., et al., "Experimental Evaluation of Operating Variables in Contact Flocculation", Jour. Amer. Water Works Assoc., 63: 41 (1971).
- 22) Habibian, M.J. and O'Melia, C.R., "Particles, Polymers, and Performance in Filtration", J. San. Engr. Divn., ASCE, 101: EE5: 567 (1975).
- 23) Tate, C.H., et al., "Pilot Plant Tests of Direct Filtration", Jour. Amer. Water Works Assoc., 69: 379 (1979).
- 24) Hutchison, W.R., & Foley, P.D., "Operation and Experimental Results of Direct Filtration", Jour. Amer. Water Works Assoc., 66: 79 (1974).
- 25) Hutchison, W.R., "High-Rate Direct Filtration", Jour. Amer. Water Works Assoc., 68: 292 (1976).
- 26) Glaser, H.T., & Edzwald, J.K., "Coagulation and Direct Filtration of Humic Substances with Polyethylemine", Environmental Science & Technology, 13: 299 (1979).
- 27) Stump, V.L., "The Use of Synthetic Polymers in Water Treatment", Ph.D. Thesis, University of Missouri-Columbia, Missouri (1977).
- 28) Treweek, G.P., "Optimization of Flocculation Time Prior to Direct Filtration", Jour. Amer. Water Works Assoc., 71: 96 (1979).
- 29) O'Melia, C.R. and Stumm, W., "Theory of Water Filtration", Jour. Amer. Water Works Assoc., 59: 1393 (1967).
- 30) Spielman, L.A., and Cukor, P.M., "Deposition of Non-Brownian Particles Under Colloidal Forces", Jour. Colloid Interface Sci., 43: 51 (1973).
- 31) Herzig, J.R., Leclerc, D.M., and LeGoff, P., "Flow of Suspensions Through Porous Media", Ind. Eng. Chem., 62: 8 (1970).
- 32) Spielman, L.A., and Fitzpatrick, J.A., "Theory of Particle Collection Under London and Gravity Forces", Jour. Colloid Interface Sci., 42: 607 (1973).
- 33) Ghosh, M.M., Jordan, T.A., and Porter, R.L., "Physicochemical Approach to Water and Wastewater Filtration", Jour. Env. Eng. Div., Proc. Amer. Soc. Civil Engr., 100: EE1, 71 (1975).
- 34) Jordan, T.A., Ghosh, M.M., and Boyd, R.H., "Physicochemical Aspects of Deep-Bed Filtration", Jour. Water Poll. Control Fed., 46: 2745 (1974).
- 35) Wnek, W.J., et al., "The Role of Colloidal Chemistry in Modelling Deep-Bed Liquid Filtration", Chem. Engr. Sci., 30: 1035 (1975).

- 36) Tien, C., et al., "Simulation of the Dynamic Behavior of the Deep-Bed Filters", AICHE Journal, 25: 3: 385 (1979).
- 37) Pavoni, J.L., and Echelberger, W.R., Jr., "Coagulation Control Using Electrical Conductivity", Water Sew. Wks., 118: 17 (1971).
- 38) Adin, A., et al., "The Application of Filtration Theory to Pilot-Plant Design", Jour. Amer. Water Works Assoc., 71: 17 (1979).
- 39) PEI Polymers, Dow Chemical Company, Midland, Michigan 1974.
- 40) Zimm, B.H., "Apparatus and Methods for Measurements and Interpolation of the Angular Variation of Light Scattering, Preliminary Results on Polystyrene Solutions", Jour. Chem. Phys., 16: 1099 (1948).
- 41) Gregory, J., Jour. Colloid & Interface Sci., 37: 364 (1973).

APPENDIX

1. Calculation of G in Clogging Filter

$$G = \left(\frac{Q_o \rho_s g h}{f A L \mu} \right)^{1/2}$$

$$= \left(\frac{A V_o \gamma_s h}{f A L \mu} \right)^{1/2}$$

$$= \left(\frac{V_o \gamma_s h}{f L \mu} \right)^{1/2}$$

Q_o = flowrate, ft³/s

V_o = superficial area, sf

L = filter depth, ft

A = filter area, sf

f = porosity

h = headloss, ft

μ = viscosity, lb-sec/sf

γ_s = specific weight of suspension

$= \gamma_{\text{water}} = 62.4 \text{ lb/cf}$

G = velocity gradient, sec⁻¹

P_s = density of suspension, lb-sec²/ft⁴

g = gravity acceleration, ft/sec²

Assuming a temperature of 27°C, $f=0.42$, $V_o=3 \text{ gpm/sf}$, $L=1.5''$, $\gamma_s=62.4 \text{ lb/cf}$

$$G = 717 h^{1/2}$$

Alternatively, we can consider filter voids connected to form capillaries.

Hagan-Poiseuille Equation

$$\frac{Q}{n} = \frac{\rho g h}{L} \cdot \frac{\pi r^4}{8 \mu} \quad (1)$$

$$\begin{aligned}
 V &= \text{Vol of voids of capillaries} \\
 &= \pi r^2 L n \\
 n &= \text{no. of capillaries with radius, } r
 \end{aligned} \tag{2}$$

From Eq (1) & (2):

$$r^2 = \left(\frac{8\mu L Q}{\rho g h \pi n} \right)^{1/2} \tag{3}$$

so,

$$V = \pi \left(\frac{8\mu L Q}{\rho g h \pi n} \right)^{1/2} L n \tag{4}$$

$$= \left(\frac{8\mu Q \pi n}{\rho g h} \right)^{1/2} L^{3/2} \tag{5}$$

But,

$$G = \left(\frac{Q \rho g h}{V \mu} \right)^{1/2} \tag{6}$$

From (5) and (6)

$$G = C h^{3/4}$$

$$C = \left(\frac{\rho g}{\mu L} \right)^{3/4} \left(\frac{Q}{8\pi n} \right)^{1/4} \tag{7}$$

Using the values suggested method 1

$$G = 506 h^{3/4} \tag{8}$$

where $L = 6''$ was used.

2. Calculation for Relationship Between G and Speed of Rotation, N.

$$P = \frac{2\pi NT}{60}$$

$$= \frac{1}{2} C_D \rho A V_p^3$$

N = rpm

T = Torque, ft-lb

P = Power, ft-lb/s

A = paddle area

$$V_r = V_p - V_{\text{fluid}} = (1-k) V_p$$

$$V_p = \text{Velocity of Paddle} = \frac{2\pi r N}{60}$$

k = Ratio of fluid velocity to paddle velocity

r = Paddle radius

So,

$$T = \left[\frac{2\pi^2}{(60)^2} \cdot C_D P (1-k)^3 r^3 A \right] N^2$$

$$= CN^2 \quad (1)$$

$$\log T = \log C + 2 \log N$$

$$\text{Plot } \log T \text{ versus } \log N \quad (2)$$

$$G = \left(\frac{P}{V_{\mu}} \right)^{1/2}$$

$$= \left(\frac{2\pi NT}{60} \cdot \frac{1}{V_{\mu}} \right)^{1/2} \quad (3)$$

From (1) and (3)

$$G = \left(\frac{2\pi N}{60} \cdot CN \cdot \frac{1}{V_{\mu}} \right)^{1/2} \quad (4)$$

For a given mixing vessel

$$G = C_1 N^{3/2} \quad (5)$$

Plot $\log G$ vs. $\log N$, slope = 1.5.